

***United States Court of Appeals  
for the Second Circuit***



**DEFENDANT'S  
EXHIBITS**



# 74-1050

## United States Court of Appeals

For the Second Circuit.

THE GENERAL TIRE & RUBBER COMPANY,  
*Plaintiff-Appellant,*

*v.*

JEFFERSON CHEMICAL COMPANY, Inc.,  
*Defendant-Appellee.*

### DEFENDANT'S EXHIBITS.

Pages 839a to End. (corrected)

WATSON LEAVENWORTH KELTON & TAGGART,  
*Attorneys for Plaintiff-Appellant,*  
100 Park Avenue,  
New York, N. Y. 10017  
(212) 683-4221.

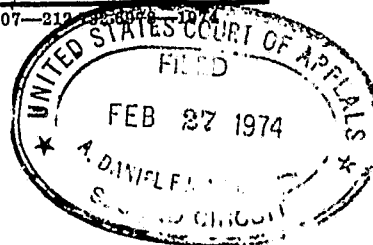
KANE, DALSIMER, KANE, SULLIVAN & KURUCZ,  
*Attorneys for Defendant-Appellee,*  
420 Lexington Avenue,  
New York, N. Y. 10017  
(212) 532-9400.

#### *Of Counsel:*

JAMES R. SWEENEY,  
J. ROBERT STAPLETON,  
COFFEE AND SWEENEY,  
20 North Wacker Drive,  
Chicago, Ill. 60606

THE REPORTER COMPANY, INC., New York, N. Y. 10007—212 683-4221

(3097)



DEFENDANT'S EXHIBIT A

U. S. Patent No. 2,866,774, Charles C. Price

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 2,866,774

December 30, 1958

Charles C. Price

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 62, strike out "propylene oxide and about .01 to 10 mol percent based" and insert instead -- 600, and (2) at least about an equal molar amount based --.

Signed and sealed this 23rd day of June 1959.

(SEAL)  
Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON  
Commissioner of Patents

## United States Patent Office

2,866,774

Patented Dec. 30, 1958

1

2,866,774

## POLYETHER POLYURETHANE RUBBER

Charles C. Price, South Bend, Ind., assignor to University of Notre Dame, Notre Dame, Ind., a non-profit institution

No Drawing. Application September 23, 1953  
Serial No. 381,999

12 Claims. (Cl. 260-77.5)

This invention relates to rubbery reaction products of organic di-isocyanates and high molecular weight polyglycols which have unusual physical characteristics.

Rubbery reaction products of polyesters, such as the polyesters formed by reacting adipic acid and ethylene glycol to high molecular weight, are well-known and have excellent physical properties when properly prepared. All of the polyesters, however, are hydrolyzable in water and the greater the proportion of ester groups the greater is the susceptibility toward hydrolyzation. Since the rubbery polyester-polyisocyanate reaction products do not have the resistance to water that is desired, they cannot be employed in many applications for which they are otherwise fairly suited.

The polyethers have considerably greater stability against hydrolysis than have the polyesters and for this reason attempts were made to form rubbery products from them. Attempts to utilize polyethers such as the polyglycols for reaction with di-isocyanates, for example, polyethylene glycol including di- and tri-ethylene glycol, polypropylene glycol including di- and tri-propylene glycol and similar low molecular weight polyglycols, yielded nylon-like products which could be cold drawn into fibers and the like but which had few if any rubbery properties.

An object of this invention is to provide vulcanizable elastomeric polymerization products of polyglycols and organic di-isocyanates having superior physical properties, particularly high abrasion resistance, good flexibility at low temperatures, and good modulus, tensile strength, and elongation characteristics.

Other objects and advantages will be apparent from the following description of my invention.

I have found that vulcanizable, rubbery polymerization products can be formed by reacting high molecular weight polyglycols containing some alkylene oxide units having at least three carbon atoms with organic di-isocyanates or di-carboxylic acids.

While it has heretofore been considered desirable that rubbery materials be produced from polymer molecules which are essentially linear, I have found when the molecular weight is sufficiently high, linear molecular structure is unnecessary. Although it is preferred to have an entirely linear glycol for reaction with the di-isocyanate or di-carboxylic acid, it has until recently been difficult to obtain sufficiently high molecular weight linear polyglycols and I have found the deficiency in a molecular length of linear polyglycols may be balanced by increasing the molecular weight of the polyglycol by a branching operation in which a very small amount of a tri- or tetrahydric alcohol is incorporated in the glycol forming materials. When a small amount, 5 percent or less and preferably around .01 to 1 mol. percent, of an alcohol having more than 2 primary hydroxyl groups such, for example, as pentaerythritol is incorporated with propylene oxide or with a polypropylene oxide of comparatively high molecular weight, one obtains essentially a glycol having a molecular weight several times as high

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as the linear glycol obtained with the propylene oxide but with some branching in the chain thereof. Such a glycol surprisingly yields, when treated with di-carboxylic acids and di-isocyanates of a suitable type, rubbery reaction products having exceptionally desirable characteristics.

For corresponding structure the polyurethan is more resinous than the polyester. Therefore when a di-isocyanate is used as a corresponding agent for the polyglycol the molecular weight in the polyglycol must be somewhat higher or the amount of branching in the polyglycol must be less than when a polycarboxylic acid or its ester is used as a condensing agent.

As before mentioned, both the molecular weight of the glycols and the amount of branching makes considerable difference in the character of the products obtained. In the case of the linear polyglycols molecular weights as low as 600 are found to yield good rubbery products when suitably treated with a given di-isocyanate. When the glycol has substantial percentage of pentaerythritol, trimethylol propane or aliphatic alcohol having three to six primary hydroxyl groups added to the condensing materials, the molecular weight of the polyglycol required for formation of good plastic rubbery products become progressively higher as the amount of pentaerythritol or other such aliphatic polyhydric alcohol is increased although rubbery material was obtained with a molecular weight as low as 600. Only a very small amount of polyhydric alcohol having three to six primary hydroxyl groups need be present in the glycol in order to greatly increase the molecular weight of the product. If the essential linearity required for the formation of a rubbery reaction product is to be maintained, the percentage of polyhydric alcohol with three to six hydroxyls (preferably primary) in all cases should be less than 10 mol. percent of trimethylol propane or equivalent considering the number of hydroxyls in the molecule. It preferably should not exceed 1 or 2 mol. percent of the units obtained from the dihydric alcohol or alkylene oxide.

As one increases the amount of polyhydric alcohol having three or four or more primary hydroxyl groups therein, the reaction products become first less plastic, although still rubbery, and then as the proportion of the polyhydric alcohol is further increased the reaction products become resinous. Furthermore, the amount of hardening is in direct ratio to the amount of primary hydroxyls in the aliphatic alcohol. The amounts of an alcohol with four hydroxyls needed to obtain a given hardness is smaller than the amount of tri-hydroxyl alcohol needed to obtain the same hardness. A mole of pentaerythritol is equivalent to approximately 1 1/4 mols of trimethylol propane in this respect. If the reaction product is to be used in making sponge which is cured as it is formed to entrap the carbon dioxide released in the reaction, the amount of an alcohol such as pentaerythritol present in the polymer may be increased up to as high as 10 mol. percent of the alkylene oxide units to provide a cured or cross-linked structure. A small amount of water and excess isocyanate is added for the purpose of effecting the desired reaction in the formation of sponge. Otherwise, percentages of pentaerythritol below 5 percent are preferred.

In accordance with the present invention, I have also found that polymeric materials built with alkylene oxide units having at least three carbon atoms, such as propylene oxide units, are far superior to those built with ethylene oxide units because the resultant rubbery product has improved water resistance and less tendency to crystallize. Propylene oxide units or other alkylene units having at least three carbon atoms incorporated in a polymer of sufficiently high molecular weight are required to give

the product of the present invention. It is not essential, however, that the entire alkylene oxide chains of the glycol be made up of alkylene oxide units, having at least three carbon atoms for it is found that the presence of relatively small proportions of propylene or high carbon atoms oxide units break up the regularity of the structure sufficiently to give rubbery products. The water resistance is, however, decreased as the amount of the propylene or higher alkylene oxide is decreased. As little as 15 or 20 percent of propylene oxide and/or higher alkylene oxide such as butylene oxide units or the like gives rubbery products of increased water resistance and less crystallinity when suitably reacted with di-isocyanates.

The polyglycols contemplated by this invention include polypropylene glycols, polybutylene glycols, other polyalkylene glycols formed from alkylene glycols having three or more carbon atoms and mixed polyglycols having at least 20 percent (preferably more) of propylene oxide units of 3 or more carbon atoms which polyglycols are characterized by being linear and by having a molecular weight of at least 600, as well as the condensation products of pentaerythritol and polyglycols preferably having less than 5 percent pentaerythritol and a molecular weight of at least 1000 and preferably at least 1500. Polypropylene and mixed propylene and ethylene glycols of 1000 molecular weight have recently become available commercially and the higher polyalkylene glycols of sufficiently high molecular weight may be made by condensing the alkylene oxide with pentaerythritol as already described.

While the high molecular weight polyalkylene glycols formed from copolymerization of ethylene oxide and propylene oxide and the like to give a mixed high molecular weight polyethylene-polypropylene glycol or high molecular weight polypropylene glycols are preferred for reaction, the high molecular weight polyethylene glycols and polypropylene glycols can be mixed together and the resultant polyglycol mixture employed. In any case, the polymer for reaction with the di-isocyanate should preferably have a molecular weight of over 1000 especially when the amount of branching is substantial.

The organic di-isocyanates suitable for use with this invention include *m*- and *p*-phenylene di-isocyanate; toluene di-isocyanate; *p,p'*-diphenyl di-isocyanate and substitution products thereof such as *p,p'*-diphenyl-3,3'-dimethyl (or -dimethoxy) di-isocyanate; 1,5-naphthylene di-isocyanate; 4,4-diphenylmethane di-isocyanate; and tetra-, penta-, hexa-, hepta- and octamethylene-*o,o'*-di-isocyanate. Both aromatic and aliphatic di-isocyanates can be used. The aliphatic di-isocyanates, however, are more toxic and for this reason are not preferred. Mixtures of diisocyanates and tri-isocyanates may also be used but the amount of tri-isocyanate, such as *p,p',p''*-triphenylmethane tri-isocyanate used should be limited to prevent excessive cross-linking and formation of hard, resinous polymers. The more trifunctional isocyanate present the less is the plasticity in the final product. In this respect the trifunctional isocyanates are similar in effect to the proportion of pentaerythritol in the polymer. Organic isothiocyanates, such as *p,p'*-phenylene di-isothiocyanate may also be used.

In place of an organic di-isocyanate, I can use any ester forming dicarboxylic acid, or its anhydride or ester such as sebacic acid, phthalic or glutaric anhydride, adipic acid, dichethyl malonate, diethyl phthalate, terephthalic acid, oxodibutyric acid or the like.

Since the reaction between a polyglycol and di-carboxylic acid is not as fast as the reaction between a polyglycol and organic di-isocyanate, the polyglycols and the di-carboxylic acid should be reacted at elevated temperature to eliminate any water evolved in the reaction and therefore drive the reaction nearer completion.

At least part of the reaction between the polyglycol and the di-isocyanate occurs rapidly at room temperature. When both isocyanate groups are of equal reactivity set up in the polymer is likely to occur before it can be han-

dled. This difficulty is reduced by using isocyanates such as toluene diisocyanate with groups of different reactivity. Di-isocyanate dimers may also be used in place of the di-isocyanate to slow down the reaction rate.

The following examples further illustrate my invention.

#### EXAMPLE 1

100 parts of Ucon fluid 75-H-1400 (a polyglycol copolymer of 75 parts of ethylene oxide and 25 parts of propylene oxide having two terminal hydroxyl groups, a molecular weight of 2000, and being sold by the Carbide and Carbon Chemicals Division of Union Carbide and Carbon Corporation of New York, New York) was heated with 20 parts of TDI (2,4-toluene diisocyanate) at 150° C. for ten minutes. It was then allowed to cool to about 60° C. at which time the viscosity of the mixture was about the same as honey.

The mixture was placed in a Day mixer (a powerful double bladed kneader) and 6 parts of water were added. Upon the addition of water, carbon dioxide was evolved and the viscosity of the mix increased until finally a rubbery material was formed. This was removed from the mixer and placed on a rubber mill. 42 parts of carbon black, 2 parts of paraformaldehyde and 1 part of salicylic acid were milled in and the rubber stock was placed in a mold and cured for 30 minutes at 310° F. The resulting sheet was well cured and had excellent properties. Tensile strengths in excess of 2800 p. s. i. were obtained.

#### EXAMPLE 2

Pentaerythritol was reacted with sodium to form the corresponding sodium alcoholate. Propylene oxide and the pentaerythritol were combined in a mol. ratio of 100 mols of propylene oxide to 1 mol. of pentaerythritol alcoholate. On heating at about 75° C. a dark brown, sticky, gummy polymer formed in approximately 20 minutes. 100 grams of polymer were then reacted with 15 grams of diethyl phthalate at around 140° C. to give an elastomeric polymer.

#### EXAMPLE 3

1 mol. of propylene oxide (70 cc.), .05 mol. of pentaerythritol (6.8 grams) and about 1.5 gram of sodium were placed in a pressure reactor at 142 to 150° C. This formed a viscous brown polymer. 100 grams of polymer were dissolved in alpha-chloro naphthalene and 15 grams of TDI were added to the polymer. At the end of about 15 minutes a dark brown elastomer was formed.

#### EXAMPLE 4

1 mol. of Ucon 74-H-1400 was condensed with 1/4 mol. of MDI (*p,p'* diphenyl methane di-isocyanate) for approximately 5 minutes and was condensed with .65 mol of TDI in the presence of 1/4 mol. of tri-ethylamine. This formed a viscous honey-like material. This was finally reacted with .56 mol of water to form rubbery polymer.

The polymer was compounded as follows:

	Grams
Polymer .....	250
Carbon black .....	125
Paraffin .....	5
Salicylic acid .....	2
Paraformaldehyde .....	1

This compound was cured for 45 minutes at 260° F. The following properties were obtained, as compared with Paracril 18-80 (a butadiene-acrylonitrile rubber manufactured by the U. S. Rubber Company).

Table I

	RM-7B	Paracril 18-80
Tensile Strength.....	2,470	2,200
300% Modulus.....	2,880	2,200
Elongation (Percent).....	580	410
Hardness.....	70	68

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Table I—Continued.

VOLUME INCREASE AT ROOM TEMPERATURE FOR 48 HOURS (PERCENT)

	RM-7B	Paracril 19-80
Hexane.....	19	19.5
Benzene.....	40.8	172
Acetone.....	0	18.5
Water.....	173	9.5

LOW TEMPERATURE FLEXIBILITY—GEHMAN TR TEST

Retraction at—	° C.	° C.
10%	-32	-36.5
20%	-30	-34
30%	-28	-32.5
40%	-26.5	-31.0
50%	-25	-30.5
60%	-24	-30

Heat Resistance.....	8 hours @ 220° F.	24 hours @ 220° F.	8 hours @ 220° F.	24 hours @ 220° F.
Tensile Change.....	Percent -64	Percent -31	Percent -82	Percent -15
Elongation Change.....	-34	-25	-25	-21
Point Hardness Change.....	-9	-2	8	4

## EXAMPLE 5

100 grams of Pluronic L62 (a mixed polyethylene-polypropylene glycol polymer with terminal hydroxyl groups, having molecular weight of 2000, and being manufactured by the Wyandotte Chemical Corporation of Wyandotte, Michigan) were mixed with 18 parts of TDI at 180° C. for a few minutes and the resulting product was reacted with water to give a superior elastomeric polymer similar to those of the preceding examples.

The polyglycols are believed to be made up of high molecular weight polymers made up of propylene, ethylene, or other alkylene units attached to one another through an ether linkage and are provided with terminal hydroxyl groups. The polymers built up from propylene oxide units or other alkylene oxide units are somewhat similar to the polyglycols except that they are built from chain starters such as pentaerythritol or trimethylol propane. These polymers are also believed to contain terminal hydroxyl groups.

The polyglycols and di-isocyanates are combined on approximately an equimolar basis. Generally from 5 to 25 and preferably from 10 to 20 parts of di-isocyanate are used for each 100 parts of polyglycol. When the elastomer is too soft and gummy, additional di-isocyanate is added and when it is too hard and resinous, less isocyanate should be added. The polyglycol should preferably be heated prior to the reaction at least until it is in liquid form.

It is to be understood that in accordance with the provisions of the patent statutes, variations and modifications of the invention described herein may be made without departing from the scope of the invention.

Having thus described my invention, what I claim is:

1. A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) a hydroxy terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide having from 2 to 4 carbon atoms and about .01 to 10 mol. percent based on the alkylene oxide of a polyhydric alcohol having less than 7 carbon atoms and having 3 to 6 primary hydroxyl groups, at least 20 percent of said alkylene oxide having more than 2 carbon atoms, and (2) at least about an equal molar amount of an organic diisocyanate based on said polyether glycol, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether glycol polymer is formed.

2. The process of claim 1 in which the reactants are heated from 100 up to 200° C. and wherein the said polyhydric alcohol is about 1 to 5 mol percent of the said alkylene oxide.

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3. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of propylene oxide and about .01 to 10 mol percent based on the propylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 6 hydroxyl groups, said condensation product having a molecular weight of at least 600 and (2) at least about one mole per mol of condensation product of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

4. A process of preparing a polyurethane reaction product comprising the steps of mixing (1) a liquid hydroxyl terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide of 2 to 4 carbon atoms inclusive, at least 20 percent of said alkylene oxide having more than 2 carbon atoms and about .01 to 10 mol percent based on the alkylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 6 hydroxyl groups and (2) at least an equal molar amount based on said condensation product of an organic polyisocyanate having 2 to 3 functional isocyanate groups, and reacting the mixture to form a reaction product having a chain length substantially greater than that of said polyether glycol polymer.

5. A process of preparing a polyurethane reaction product comprising the steps of mixing (1) a liquid hydroxyl terminated condensation product of an alkylene oxide having 2 to 4 carbon atoms of which at least 15 percent is propylene oxide and about .01 to 5 mol percent based on the alkylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 6 hydroxyl groups, said condensation product having a molecular weight of at least 600, and (2) an excess of an organic polyisocyanate having 2 to 3 functional isocyanate groups over that required for reaction with the hydroxyl terminal groups of the condensation product, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

6. A product made according to process of claim 1.

7. A product made according to process of claim 2.

8. A product made according to process of claim 4.

9. A product made according to process of claim 5.

10. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a first polymer comprising a condensation product of about 100 parts by weight of propylene oxide and about .01 to 10 mol percent based on the propylene oxide of pentaerythritol, said first polymer having a molecular weight of at least 600, and (2) at least about an equal molar amount based on the amount of said condensation product used of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said first polymer is formed.

11. A process of forming a polyurethane comprising the steps of mixing (1) a condensation product of propylene oxide and about .01 to 10 mol percent based on the propylene oxide of trimethylol propane, said condensation product having a molecular weight of at least 600 and about .01 to 10 mol percent based on the amount of said condensation product used of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

12. A polyurethane reaction product of (1) about one mole of an organic diisocyanate and (2) about one mole of a condensation product of an alkylene oxide of 2 to 4 carbon atoms of which at least 15 percent is propylene oxide, and about .01 to 10 mol percent based on the alkylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 4 hydroxyl groups, said condensation product being hydroxy terminated and having a molecular weight of at least 600, said polyure-

thane reaction product having a chain length substantially greater than that of said condensation product.

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DEFENDANT'S EXHIBIT C

Price, C., "How Chemists Create a New Product",  
The Chemist, April 1961

Pages 844a to 849a



844a

Return to UPCHURCH

The Birth of  
Poly (propylene oxide)  
Rubber

## How Chemists Create a New Product

Dr. Charles C. Price, F.A.I.C.

Blanchard Professor of Chemistry and Chairman of the Department of  
Chemistry, University of Pennsylvania, Philadelphia, Pa.

(Address given when the author received the Honor Scroll of the Philadelphia AIC  
Chapter, Feb. 2, 1961, in Philadelphia, Pa.)

THIS is the story of the creation and development of a basically new type of synthetic rubber, differing radically from natural and conventional synthetic rubbers in having oxygen atoms built into the polymer chain sequence. In addition to the fundamental scientific concepts and the important ways this idea has affected my research activities, one practical embodiment is a superior foam rubber now being produced at a rate approaching 100,000,000 lbs. per year, scarcely three years after its commercial debut; another may become the basis for a new type of first-class tire rubber.

In the Fall of 1948, the National Academy of Science Quartermaster Advisory Committee on Elastomers was concerned with developing new approaches in the search for superior new rubbery materials serviceable at low temperatures and resistant to organic solvents. We thought that new approaches might result from leisurely discussion by a small group of chemists and physicists acquainted with pertinent kinetic and thermodynamic concepts. I agreed to organize such a meeting, which was held in Washington the last three days of Jan. 1949. The group included: Drs. John G. Aston, William O. Baker, C. S. Fuller, Peter J. Debye, F.A.I.C., Paul J. Flory, George E. Kimball, M. Mooney, R. H. Ewart, Kenneth S. Pitzer, F.A.I.C., W. B. Reynolds, Frederick D. Rossini, F.A.I.C., R. Simha, F.A.I.C., L. A. Wood and F. T. Wall.

From this fruitful discussion many specific recommendations were passed on to a larger meeting representing most of the elastomer research teams in universities, government, and industry. The basic concepts of a rubber structure were formulated as a three-dimensional, net-work structure with long-chain, randomly-coiled segments of polymer between cross-links. For these chain segments to permit rubbery properties, the chains must be able to coil and uncoil readily from thermal energy available at the ambient temperature of use. This requirement imposes the conditions that the units of the polymer chain must (1) have low intrachain barriers to rotation, (2) have low interchain Van der Waal's forces (so that chains can readily slip past one another during stress and relaxation) and (3)

Copies sent to Mr. Wilson + Dr. Saunders on 4-11-61  
Dr. Darnach on 4-19-61, Mr. Mocher on 5-8-61.

have sufficient dissymmetry to prevent crystallization of chain segments at use temperatures.

It struck me that a chain segment meeting these requirements was that derived from polymerization of propylene oxide, and this idea was incorporated in the recommendations of the conference. The oxygen atom in the chain would contribute greatly to the flexibility, since the barrier to rotation at carbon-oxygen bonds (1200 cal./mole) was much less than that for carbon-carbon bonds (2800 cal./mole in ethane). Ethers have relatively low "cohesive energy" densities between molecules, so interchain "stickiness" would be expected to be low. Since even relatively low molecular weight poly(ethylene oxide) was a crystalline solid (m.p. ca. 65°), while polymers of propylene oxide of molecular weight near 2000 were liquids at temperatures down to or below -50°C., the methyl group in the latter evidently conferred the necessary dissymmetry to obstruct crystallinity. The extra methyl group would also be expected to confer greater resistance to dissolution or swelling by water.

On returning to Notre Dame, a look at the literature revealed obstacles to preparation from poly(propylene oxide) of the kind of long segment network structure essential for rubbery properties. Whereas Prof. Staudinger had reported poly(ethylene oxide) with a molecular weight of 20,000<sup>1</sup>, there were no reports of poly(propylene oxide) with a molecular weight over a few thousand, among many disclosures of polymerization conditions and catalysts. Elucidation of the reason for this remarkable difference between ethylene and propylene oxides were the basis for many years of research by my students, but the fact obstructed preparation of a rubber network by the conventional procedures of vulcanization, involving crosslinking relatively high-molecular weight linear polymer.

Another approach of promise occurred to me. It involved preparing low-molecular weight poly(propylene oxide) with two or more terminal hydroxyl groups and then using these reactive groups to build up the necessary molecular weight and network structure.

Since "Vulcollan" had been announced by the Bayer Co., involving the conversion of low molecular weight polyesters terminated by hydroxyl groups to rubber by reaction with polyfunctional isocyanates, a similar approach was considered for the initial effort with polyether glycols. By varying the molecular weight of the polyglycol reactant, as well as the ratio of diol to polyol component in the polyglycol, one can vary the distance between crosslinks at will.

Ralph Herbst, who had finished his thesis on the kinetics of benzoyl

## HOW CHEMISTS CREATE ...

peroxide decomposition with me in March 1949, was invited to begin work at Notre Dame on this approach, with some financial support kindly supplied by General Tire & Rubber Co. as a supplement to my fellowship program with them. Almost his first experiments involved sodium-catalyzed polymerization of propylene oxide containing 5 mole-% of pentaerythritol. When this viscous liquid was treated with toluene diisocyanate, it reacted readily and exothermally to produce either hard, insoluble resins or rubbers. He showed that the poly(propylene oxide) glycol he had prepared had a molecular weight of about 650 and that he could also prepare rubbery products from it by reaction, not only with diisocyanates, but also through ester groups with succinic, maleic and several other dibasic acids. He also prepared a rubbery polyurethan from linear poly(propylene oxide) glycol.

Various aspects of this were explored further at General Tire, especially by Dr. Charles E. Greene. The concept and supporting experimental results were submitted as a patent application in 1953. Claims covering the linear glycol polyurethan and the branched chain glycol polyester were disallowed, but the patent issued 30 Dec. 1958, with claims covering products made from branched poly(propylene oxide) glycol with a minimum molecular weight of 600 and containing 0.1 to 5% or 0.1 to 10% of a polyhydric alcohol such as glycerol or pentaerythritol.<sup>2</sup>

Sometime before our patent issued, several companies developed extremely useful and practical procedures for making an excellent flexible polyurethan foam by a "one-shot" process utilizing poly(propylene oxide) of approximately 2000 molecular weight prepared with 2-3% of glycerol. This process has been dramatically successful. Production in 1960 was estimated at 75,000,000 pounds with further expansion expected.

Two other important patent developments relevant to the development of poly(propylene oxide) polyurethan rubber, were: An American patent issued Aug. 9, 1960, to Windemuth, Schnell & Bayer<sup>3</sup>, filed in Germany, 10 May 1951, and assigned to Mobay and to Bayer. This patent claims products and processes of condensation of diisocyanates with poly(alkylene ethers) with at least two hydroxyl groups per molecule and of molecular weight above 500. While the claims cover all poly(alkylene oxides), the disclosure and examples mention only poly(ethylene oxide). These German chemists were working in a laboratory which led the world in developing polyester polyurethans. In a patent filed over two years after our conception and reduction to practice, they had clearly failed to recognize the significant advantages of the propylene oxide unit over the ethylene oxide unit in decreasing water sensitivity and crystallization.

On the basis of an application filed by Saunders and Heiss a few weeks before ours, Mobay has been allowed to copy some of our claims (0.1-10% polyol) but not others (0.1-5% polyol) and an interference was declared on this basis some months after our patent issued. This interference has so far obstructed enforcement of even the uncontested claims of our patent. The basis of the interference were several examples encompassing branched-chain poly(propylene oxide) stated to be a condensation product of 13.2 moles of propylene oxide with one mole of glycerol, which was then condensed with a diisocyanate. The issue has not yet been resolved by the Board of Interferences. We feel that the Saunders and Heiss application lacks, either explicitly or inherently, the basis of meeting the 600 molecular weight limitation on the polyglycol of our claims. Our date of conception was 2 years earlier than that of Saunders and Heiss; our first preparation of polyurethan rubber was 4 years earlier. We believe there is justifiable optimism for a favorable ruling—a biased conjecture!

Less controversial scientific facets of propylene oxide polymerization have received much attention in the past ten years: First was the initially frustrating refusal of propylene oxide to produce polymer of nearly as high molecular weight as had been obtained with ethylene oxide. With hot sodium hydroxide, polymer with a molecular weight of 1000 or two was obtained. With acid catalysts the situation was worse—molecular weights were only a few hundred. By accident, Leon St. Pierre, working with me, discovered that potassium hydroxide would catalyze the polymerization even at room temperature, to give polymer of 4000-6000 molecular weight.<sup>4</sup> We were surprised to find that this liquid polymer, which we presumed to be a diol, gave almost no change in viscosity on treatment with diisocyanates. It was surprising to find that samples of liquid polymer made by hot alkali polymerization and sold by a major poly(propylene oxide) producer as material terminated at one end by hydroxyl and the other by alkoxyl, thus presumably monofunctional, gave excellent rubber on treatment with diisocyanates! The answer to these riddles came from establishment of the importance of a chain-transfer process involving attack on the methyl hydrogen of the monomer . . . This incorporates allyl ether end groups at one end of polymer chains, as demonstrated unequivocally by St. Pierre<sup>4</sup>.

The next puzzle was what happens to eliminate these groups in the hot alkaline polymers? The key to this was the discovery by Dege, Harris and MacKenzie<sup>5</sup> indicating that, when polymer prepared by sodium hydroxide catalysis at 150° was isolated without hydrolysis, *cis*-propenyl

## HOW CHEMISTS CREATE . . .

ether groups were incorporated. We have now demonstrated that this group arises from base-catalyzed rearrangement of allyl ethers to *cis*-propenyl ethers. For example, in dimethyl sulfoxide as a solvent, even at room temperature, potassium *t*-butoxide will rearrange phenyl allyl ether in minutes to 99 + % yield of phenyl *cis*-propenyl ether.<sup>6</sup> The ready hydrolytic conversion of propenyl ethers to alcohols and propionaldehyde is established in the literature.

Another facet of propylene oxide polymerization which piqued curiosity was the opportunity it offered to explore the long unanswered question of the effect of configuration of asymmetric centers along a polymer chain on the physical properties of the polymer. In contrast to vinyl polymers, the asymmetric center of poly(propylene oxide) is already present in the monomer.

Using such optically-active monomer,<sup>7,8</sup> Dr. Masch Osgan<sup>9</sup> discovered that a new type of poly(propylene oxide) was formed, not a liquid as from ordinary DL-monomer, but a crystalline solid. This discovery, concurrent with the discovery of crystalline polypropylene by Prof. Natta<sup>10</sup>, gave strong support to his proposal that his new crystalline polymer also differs from earlier forms in having all the asymmetric atoms in the same configuration. In his case the isotactic arrangement had been imposed by the stereospecificity of the catalyst used for polymerization.

While our work was in progress, Pruitt and Baggett<sup>11</sup> revealed that certain iron catalysts were capable of making two new forms of poly(propylene oxide), both differing from earlier products in having much greater molecular weight, and one being a crystalline polymer, m.p. 71°. This product we showed to have identical crystalline structure to our optically active polymer<sup>9b</sup>, so the catalyst disclosed in this patent was, like Natta's, stereoselective.

Dr. Osgan<sup>12</sup>, based on our speculation about the mechanism of action of this catalyst, developed a whole family of Lewis acid type catalysts for the isotactic polymerization of propylene oxide and its analogs. These leads were further expanded by the discoveries of Prof. Furukawa<sup>13</sup> in Kyoto, and Ed. Vandenberg<sup>14</sup> at the Hercules Powder Co., of water-activated zinc and aluminum alkyl catalysts. It is now easily and economically possible to prepare homo- and co-polymers with molecular weights in excess of a million. Some years ago, Allen Noshay, working with me at Penn, showed that copolymers with unsaturated epoxides could indeed be prepared and were readily cross-linkable to rubbery material which

was swollen but undissolved by organic solvents. Since this material has low cost and superior rubber qualities, this material may have a big future—and may even become the basis for superior tires.

## REFERENCES

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- (3) E. Windemuth, H. Schnell and G. Bayer, U. S. Pat. No. 2,948,691 (9 Aug. 1960).
- (4) L. E. St. Pierre and C. C. Price, *J. Am. Chem. Soc.*, **78**, 3432 (1956).
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- (12) M. Osgan and C. C. Price, *J. Polymer Sci.*, **34**, 153 (1959).
- (13) J. Furukawa, T. Tsuruta, R. Sakata, T. Saegusa and A. Kawasaki, *Makromol. Chem.*, **32**, 90 (1959).
- (14) E. M. Vandenberg, *J. Polymer Sci.*, in press.

## Charles C. Price -- Scientist With Ideals

### Dr. Ralph Connor

Vice President in charge of Research and Chairman of the Board of Directors,  
Rohm & Haas Co., West Washington Sq., Philadelphia 5, Pa.

(Presented when Dr. Price received the Honor Scroll of the Philadelphia AIC Chapter,  
Feb. 2, 1961, Philadelphia, Pa.)

**D**R. CHARLES C. PRICE is an honest, sincere and modest person with high ideals to which he holds firmly. He has a great ability in many different types of activities and he undertakes nothing in which he does not attempt to excel.

The saying, "A prophet is not without honor save in his own country" is not always true. This is indeed, the "Country" of the Prices. Dr. Price was born in New Jersey but his family came from Swarthmore and Plymouth Meeting. Mrs. Price was raised in Lansdowne. Dr. and Mrs. Price, as their parents had done, graduated from Swarthmore and after being away twenty years, returned.

Dr. Price received the Ph.D. in 1936 from Harvard where he had worked with Prof. Fieser. He then spent 10 years at the University of Illinois, starting as research assistant to Dr. Roger Adams, and progressed through the faculty grades of instructor, assistant professor, associate professor, and professor. In 1946 he became head of the Chemistry Department of Notre Dame. He resigned 6 years later to undertake some political activities, and was then reappointed. In September 1954 he became head

DEFENDANT'S EXHIBIT D

Certified copy file history of U. S. Patent No. 2,866,774,  
Charles C. Price, Excerpts, pages 17-71

Pages 850a to 904a

850a

Doc. 17003

IN THE UNITED STATES PATENT OFFICE

3/a  
297  
MAY 1, 1954

Applicant Charles C. Price

DIVISION 50

Serial No. 381,999  
Filed September 23, 1953  
For POLYGLYCOL RUBBER

Division 50

A M E N D M E N T

To the Commissioner of Patents:

In response to the Office action of May 21, 1954,  
please amend the above-entitled application as follows:

In the specification:

Page 2, line 24, cancel the comma after "di-isocyanates"  
and insert -- of a--; same line, insert a comma after "type".

Claim 1, line 2, after "of" first occurrence, insert  
--(1)--; line 3, change "alkylene" to --polyalkylene--; line 4,  
after "and" insert --(2)--.

R E M A R K S

Until allowance of a generic claim, applicant elects  
to prosecute in this application the species of group 1  
diisocyanates including claim 2. Reconsideration of the  
rejection of claim 1 on the Pinner reference is requested. The  
claim has been amended to point out that the product claimed  
is the reaction product of a polymer principally formed from units  
of polyalkylene oxides and having a molecular weight of at least  
600 with a diisocyanate or dicarboxylic acid. As pointed out  
in the specification, a very definite result is obtained when  
polyalkylene oxides having a molecular weight greater than 600  
are reacted, than is obtained when low molecular weight alkylene  
oxides are so reacted. As shown by Pinner reference, Pinner  
obtained a Nylon-like material Perlon U. This is a hard resin.  
Applicant's materials are extremely rubbery and of varied types.



*W* The limitation of 600 molecular weight is not an idle one, and is the lowest molecular weight from which the real benefits of the invention can be obtained from the material which is reacted with the isocyanate and which consists principally of polyalkylene oxide residues. The criterion that at least 15% of the units have more than 2 carbon atoms is also very important for the reason that the two carbon atom units nest closely together whereas the three carbon atoms break up the symmetry and cause much more rubberyness. It is therefore seen that the Pinner reference, which has no disclosure of the use of any high molecular weight polyglycol or polyalkylene oxide condensate, has no relation to the claims herein.

Claim 1 has been amended to make it more apparent that the polymer<sup>a</sup> has a molecular weight of at least 600 before it is reacted with the isocyanate.

Reconsideration is also requested of the rejection of claims 1, 4 and 5 on the Breslow Patent 2,531,392. This material is varnish type material entirely different from that of applicant. There is no disclosure in this patent of the reaction of any polymer composed principally of alkylene oxide units and having a molecular weight anywhere nearly the critical 600 molecular weight. The examiner has apparently failed to appreciate the criticality of the propylene oxide units or units having three or more carbon atoms per pair of oxygen atoms in the chain. Polymers containing at least 15% of propylene oxide or higher units are much more rubbery than are polymers of ethylene oxide even though the alkylene oxide polymer without isocyanate action has a molecular weight of at least 600. Applicant's specification it is thought clearly brings out the advantage of the alkylene oxide having three or more carbon atoms so that these claims clearly distinguish from the Breslow reference in addition to specifying a molecular weight of at least 600 by specifying the critical

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proportion of propylene or higher alkylene oxide units.

Reconsideration of claims 1, 4 and 5 as unpatentable over the ICF patent 882,107 is also requested. While this patent states, as the examiner states, lines 38 to 46, that in place of the substances of relatively low molecular weight one is able to utilize the compositions of higher molecular weight, for example those composed of bifunctional linear polymers such as the polyethylene oxides or the poly 1, 4 butadiene oxides having hydroxyl groups or amino groups at their two extremes, applicant has pointed out that the molecular weight is critical in that it must be at least 600 in order to produce the rubbery material of the present invention. A higher molecular weight than the substances previously mentioned need not be anywhere near a molecular weight of 600, which is the minimum molecular weight called for by applicant's claims prior to the reaction with isocyanate. It is therefore seen that the ICF reference has no disclosure of the invention claimed herein. Polyurethanes made by reacting isocyanates with polymers of insufficient molecular weight are hard resinous materials. Applicant's products are highly resilient wear-resistant rubbers.

It is submitted that applicant's claims distinguish from all of the references no matter how combined. While it is known that one has been able to produce rubbery materials from certain polyesters, it is submitted that the preparation of rubbery materials from polyethers and particularly branch chain polyethers which are non-linear is entirely novel with applicant. An allowance of the application is solicited.

Respectfully submitted

EVANS & MCCOY  
Attorneys

Cleveland, Ohio

By J. H. L. Grottel

853a  
DEPARTMENT OF COMMERCE  
UNITED STATES PATENT OFFICE  
WASHINGTON

All communications respecting  
this application should give the  
serial number, date of filing,  
and name of the applicant.

PAPER No. 1

Charles H. Price  
1111 1/2 Building  
Akron, Ohio

Please find below a communication from the  
EXAMINER in charge of this application.

*Robert C. Watson*  
Commissioner of Patents.

Applicant: Charles H. Price	
Ser. No. 331,000	MAILED  FEB 21 1956 PAT DIV 50
Filed September 23, 1953	
For POLYGLYCOL RUBBER	

10-6847-2 GPO

Responsive to amendment filed November 4, 1954.

Additional references made of record:

Patent of Hill	2,333,206	Oct. 30, 1945	260-75	HXR
Patent of Rugg	2,567,076	Sept. 4, 1951	260-75	
Patent of Hill	2,626,915	Jan. 27, 1953	260-75	HXR
Patent of Hill	2,637,430	Aug. 24, 1954	260-75	
Patent of Langerak	2,602,374	Oct. 26, 1954	260-77.5A	
		(Filed May 17, 1952)		
Patent of Hill	2,702,707	Feb. 22, 1955	260-77.5A	
		(Filed April 10, 1953)		
Patent of Hill	2,726,219	Dec. 6, 1955	260-2.5A	
		(Filed Aug. 24, 1951)		

1. The claims are 1-7.
2. Claim 7 is rejected as informal.
3. Claims 1, 2, 4, 5 and 6 are rejected as unpatentable over each of the newly cited patents to Langerak, Hill and Rugg because pertinence is obvious; note Examples 5 and 8 of Langerak, Example 1 of Rugg and col. 2, line 5 of Hill. Note that Langerak and Hill refer to an earlier filed Hill application as abandoned and see Rule 14 (b).
4. Claims 1, 2, 4, 5 and 6 are rejected as failing to define the alleged invention properly. The polyoxide must be completely defined and "principally formed from" is not effective for such purpose. Claim 1 does not even

specify the terminal groups. The language "alkylene glycol" is indefinite. Does applicant mean "polyalkylene glycol"?

6. Claims 1, 4 and 5 are rejected as unpatentable over Cotton et al., see page 2, col. 1, lines 15-22 or De Groot, see col. 2, lines 35 et seq. The reaction of alkenes, polyalkenes and dicarboxylic acids or their equivalents are disclosed in these patents. Selection of particular temperature is not inventive. Note that in example 2, applicant actually uses an acid derivative as the acid source.

7. Claim 3 is held to be withdrawn from further consideration under Rule 142 (b) as not readable on the listed species.

8. Snow and Livengood are of interest.

Reason: 155

WJ

W.F. Bengel  
Examiner

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AUG 15 1956

DIVISION 60

DIVISION 60

IN THE UNITED STATES PATENT OFFICE

Applicant: Charles C. Price  
 Serial No: 381,999  
 Filed: September 23, 1953  
 For: POLYGLYCOL RUBBER

Division 50

A M E N D M E N T

To the Commissioner of Patents:

In response to the Office Action of February 21, 1956,  
 please amend the above entitled application as follows:

In the claims:

Claim 1, line 1, delete "An elastomeric" and substitute  
 --A--; line 2, before "polymer" insert --polyglycol--; line 3,  
 after "oxides" insert --and having hydroxyl terminal groups--;  
 line 6, after "acids" insert --, said reaction product having a  
 chain length substantially longer than that of said polyglycol  
 polymer--.

Claim 2, line 1, delete "An elastomeric" and substitute  
 --A--; line 2, delete "an alkylene polyglycol" and substitute  
 --polyalkylene glycol--; line 4, after "atoms" insert --and  
 having hydroxyl terminal groups--;

Claim 3, line 1, delete "An elastomeric" and substitute  
 --A--; line 2, delete "an alkylene polyglycol" and substitute  
 --polyalkylene glycol--; line 4, after "atoms" insert --and  
 having hydroxyl terminal groups--;

Claim 4, line 1, delete "an elastomeric" and substitute  
 --a--; line 2, after "a" insert --polyglycol--; line 5, after  
 "atoms" insert --and having hydroxyl terminal groups--; line 7  
 and 8, delete "an elastomeric" and substitute --a--; line 8,  
 after "polymer" insert --having a chain length substantially  
 greater than that of said polyglycol polymer--;

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Claim 6, line 1, delete "an elastomeric" and substitute --a--; line 2, delete "in alkylene polyglycol" and substitute --a polyalkylene glycol--; line 4, after "atoms" insert --and having hydroxyl terminal groups--; line 5, after "di-isocyanate" insert --,--; line 6, delete "elastomeric"--;

Cancel claim 7 and add the following new claims:

8. A reaction product of a polyglycol polymer having a molecular weight of at least 600 and an organic dicarboxylic acid, said polymer being formed from at least about 90 mol percent of propylene oxide and a polyhydric alcohol.
9. A reaction product of a polyglycol polymer having a molecular weight of at least 600 and an organic dicarboxylic acid, said polymer being formed from at least about 90 mol percent of an alkylene oxide having at least 3 carbon atoms and a polyhydric alcohol.
10. A reaction product of a polyglycol polymer having a molecular weight of at least 600 and an organic di-isocyanate, said polymer being formed from at least about 90 mol percent of an alkylene oxide having at least 3 carbon atoms and a polyhydric alcohol.
11. A reaction product of a polyglycol polymer having a molecular weight of 600 and being formed from propylene oxide and a polyhydric alcohol and a coupling agent selected from the group consisting of organic dicarboxylic and di-isocyanate.

Ser. No. 381,999

12. A process of preparing a reaction product comprising the steps of mixing a liquid polyglycol polymer having a molecular weight of at least 600 and being formed from at least 90 mol percent of propylene oxide and not greater than 10 mol percent of a polyhydric alcohol, and a coupling agent selected from the group consisting of organic di-isocyanates and dicarboxylic acids, and thereafter allowing the mixture to react until a reaction product is formed having a chain length substantially greater than that of said polyglycol polymer.

#### R E M A R K S

Applicant is submitting with this amendment an "Affidavit Under Rule 131" in which he shows conception and reduction to practice of the invention in this country prior to May 14, 1951 and the filing date of U. S. Patent 2,626,935 to defendant. Other references cited in this application having filing dates later than May 14, 1951 are U. S. Patent No. 2,692,874 (Langorak), 2,702,797 (Rugg) and 2,726,219 (Hill). In support of the allegations of the affidavit, applicant is submitting Exhibits A to D.

All of the experiments, work and preparations shown in Exhibits A-D were made prior to May 14, 1951 and in accordance with applicant's suggestions and under applicant's directions.

Exhibit A shows the preparation of reaction products of (1) propylene oxide-pentaerythritol polymers using a molar ratio of oxide to pentaerythritol of from 20:1 to 100:1 and (2) an organic dicarboxylic acid such as diethyl phthalate or an organic di-isocyanate such as toluene-2,4-di-isocyanate, methylene-bis-4 phenyl isocyanate.

The portion of Exhibit A directed to a polymer of propylene oxide and pentaerythritol reacted with diethyl phthalate is very similar to Example 2 of this application.

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Ser. No. 381,999

Exhibit B shows the preparation of two propylene oxide-pentaerythritol polymers by two different methods which were as follows:

- (1) A pressure reaction at 140-150°C.
- (2) A reaction at room temperature, etc.

The polymers, made under method (1) and (2) were then reacted in the absence of a solvent with organic di-isocyanates. The di-isocyanates used were toluene-2,4,-di-isocyanate, methylene-bis-4-phenyl isocyanate and octa-decyl isocyanate. The latter portion of the table in Exhibit B shows the polymer of method (1) reacted with diethyl phthalate and alpha chloronaphthalene in the presence of solvents.

Exhibit C is a letter disclosing the vulcanization of a polypropylene oxide polymer by esterification with a di-carboxylic acid such as succinic acid by heating the polymer with succinic anhydride and driving off the water evolved until gelling is accomplished. Also referred to is crosslinking of the polymer with a di-isocyanate.

Exhibit D is a progress report showing the preparation of various propylene oxide-pentaerythritol polymers with molecular weights of over 600 and in a ratio of oxide to polyhydric alcohol (pentaerythritol) of about 200 to 1 to about 10 to 1. These polyalkylene glycols were subsequently reacted with anhydride compounds such as succinyl chloride, succinyl anhydride and maleic anhydride.

In response to paragraph 4 of the Office Action of February 21, 1956 applicant has defined the terminal groups of the polyalkylene glycol as hydroxyl.

Applicant wishes to thank the Examiner for kindly pointing out that the proper terminology for the polymer should be "polyalkylene glycol." The claims have been so amended.



The patent to Boulton et al shows the formation of non-volatile ester that is useful as a plasticizer for cellulose ether films. The esterification of a polyglycol with an organic acid, which could be phthalic acid is disclosed. This polyglycol is greatly different than the reaction product of the present invention. Applicant's reaction product is formed by a polymerization reaction in which the chain length of the polyalkylene glycol polymer is substantially increased. Boulton's polyglycol ester does not substantially increase the chain length of the resultant ester over the chain length of the original polyglycol.

Claim 1, for example has been amended to include the following limitation which clearly distinguishes it from the Boulton reference: "said reaction product having a chain length substantially longer than that of said polyglycol polymer."

The hydroxyl groups only are modified in the Boulton patent. There is no increase in chain length or polymerizing of the polyglycol and the acid. In applicant's process, the organic dicarboxylic acid is a coupling agent and the chain length is substantially increased which is greatly different than merely esterifying one or two of the hydroxyl groups of the polyglycol.

It is noted that the patent to Livenood discloses the use of polyoxyalkylene glycols to form polymeric esters which differs considerably in both starting materials and final products from the instant invention.

The Snow et al patent is directed to the preparation of esters of (1) organic acids and (2) hydroxyl alkyl ethers of p-xylylene glycol. Again the starting materials and products are greatly different than those of the instant invention.

New claims, 8-12, have been added to more clearly

Ser. No. 381,999

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define the present invention.

It is submitted that all claims are now in condition  
for allowance and such allowance is solicited.

Respectfully submitted,

McCOY, GREENE & TEGROTIENHUIS  
Attorneys

BY *Richard D. Heberling*

Cleveland, Ohio

Enclosures:

Affidavit Under Rule 131  
Exhibits A-D

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AUG 20 1956

DIVISION 60

IN THE UNITED STATES PATENT OFFICE

Applicant: Charles C. Price  
Serial No: 381,999  
Filed: September 23, 1953  
For: POLYGLYCOL RUBBER

Division 50

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AFFIDAVIT UNDER RULE 131

AUG 15 1956

To the Commissioner of Patents:

DIVISION 60

Charles C. Price, being duly sworn, deposes and says he is the inventor in the above entitled application and that he conceived and reduced to practice the invention in this country prior to May 14, 1951. In support thereof affiant submits Exhibits A to D herewith.

Exhibit A, of 2 page length, is a copy of a Progress Report of Dr. Charles C. Price and Ralph L. Herbst prepared by affiant and under affiant's direction prior to May 14, 1951. This report shows the preparation of propylene oxide - pentaerythritol polymers with molar ranges of oxide to pentaerythritol of about 20 to 1 to about 100 to 1. The report further describes the reaction of these propylene oxide polymers with organic diisocyanate compounds. Another part of the report is directed to disclosure of the reaction products of a propylene oxide-pentaerythritol polymer with a dicarboxylic acid.

Exhibit B is a one page report from Charles C. Price and Ralph L. Herbst with the subject heading "Propylene Oxide-pentaerythritol Polymer". The report of Exhibit B was prepared by affiant and under affiant's direction prior to May 14, 1951 and shows the preparation of propylene oxide polymers and their subsequent reaction with organic diisocyanates and a dicarboxylic acid.

Exhibit C consists of a two page letter to Mr. T. A. TeGrotenhuis, affiant's attorney, with the date removed.

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This letter was written prior to May 14, 1951 and the experiments mentioned therein were conducted by me or under my direction before May 14, 1951. The letter describes the preparation of reaction products of propylene oxide polymers with organic diisocyanates and an organic dicarboxylic acid.

Exhibit D consists of a Progress Report entitled "Propylene Oxide-Pentaerythritol Polymer" prepared before May 14, 1951 by affiant and under affiant's direction. This exhibit shows preparation of reaction products of various propylene oxide polymers with anhydrides of organic dicarboxylic acids.

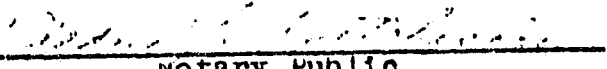
All the documents, experiments, work and preparation shown in Exhibits A-D were made prior to May 14, 1951 in accordance with my suggestions and under my direction.

Further affiant saith naught.

  
Charles C. Price

State of Pennsylvania )  
County of Philadelphia ) SS

Before me personally appeared Charles C. Price to me known to be the person described in the above affidavit, who signed the foregoing instrument in my presence, and made oath before me to the allegations set forth therein, on the \_\_\_\_\_ day of \_\_\_\_\_, 1956

  
Notary Public  
Notary Public, Philadelphia, Philadelphia Co.  
My Commission Expires March 25, 1958

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Progress Report

Subject: Propylene Oxide (1,2)-Pentaerythritol Polymer

From: C. C. Price and Ralph L. Herbst  
University of Notre Dame

Polymers have been made using

- (a) concentrated sulfuric acid as catalyst using a propylene oxide (1,2)-pentaerythritol molar ratio of 20 to 1.
- (b) sodium as catalyst using a propylene oxide (1,2)-pentaerythritol molar ratio of 100 to 1.
- (c) The reaction of (a), (b), and propylene oxide (1,2) polymers, respectively with diisocyanate compounds has been studied.
- (d) Sulfuric Acid as Catalyst

With sodium as catalyst, the reaction between propylene oxide and aliphatic alcohols has been reported to produce secondary alcohols of the following type: (1)



As catalysts such as boron trifluoride and sulfuric acid are used, a mixture of primary and secondary alcohol-ether derivatives are formed. (2) It is considered desirable, therefore, to investigate the polymer produced with sulfuric acid as catalyst. Using propylene oxide (1,2)-pentaerythritol in a molar ratio of 20 to 1 and a small amount of sulfuric acid (conc.) resulted in the formation of a dark brown, sticky gum (y) which was slightly soluble in acetone, moderately soluble in N-methyl morpholine, and insoluble in a number of other organic solvents. The reaction between (y) dissolved in N-methyl morpholine and some diisocyanate compounds (3) produced hard, brittle

(b) Using a Propylene Oxide (1,2)-Pentaerythritol Molar Ratio of 1:1 with Sodium as Catalyst.

When a molar ratio of 20 to 1 was used, the resulting polymer produced hard, brittle materials upon reaction with diisocyanates (3) - probably due to a large amount of cross-linking. The polymer formed using a ratio of 100 moles of propylene oxide (1,2) to 1 mole of pentaerythritol also produced hard, brittle polymers upon reaction with diisocyanates (3). The same reaction in the presence of diethyl phthalate produced a rubbery material.

(c) The Reaction between Propylene Oxide (1,2) Polymers and Diisocyanate Compounds (3).

Since hard, brittle polymers were still formed using a very large excess of propylene oxide (1,2) as compared to the amount of pentaerythritol used, the reaction between propylene oxide (1,2) polymer and diisocyanate compounds (3) was studied.

About 0.5 g. of sodium was added to 40 cc. of propylene oxide (1,2) and the mixture warmed gently. The reaction mixture after 20 minutes of reaction and the brown solid polymer (z) which formed after one day both gave hard, brittle polymers upon treatment with diisocyanates. The same reaction using (z) dissolved in diethyl phthalate produced a hard, rubbery material. All attempts to dissolve this rubbery material in organic solvents have failed.

REFERENCES

- (1) G. I. (2) A. I. Petrov (Tashkent Aviation Inst.) J. Gen. Chem. (U.S.S.R.) 14, 1038-43 (1944); *ibid.* 16, 1206-12 (1946); G. I. 3091 b (1947).

(3) Toluene-2,4-diisocyanate, Methylen-bis-4-phenyl isocyanate.

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Report

Exhibit B

Subject: Propylene Oxide-Pentaerythritol Polymer

From: Charles C. Price and Ralph L. Herbst

University of Notre Dame

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AUG 15 1956

DIVISION 60

## SUMMARY:

A viscous, brown polymer has been prepared by

- (1) a pressure reaction at 140-150° (N 85%)
- (2) a reaction at room temperature for three days followed by heating at 110-115° (N 90%)

In (1) and (2), 6.8 g. (0.05 mole) of pentaerythritol, 70 cc. (1.0 mole) of propylene oxide-(1,2) and about 1.5 g. of sodium were used. About 0.5 g. of unreacted pentaerythritol was recovered from (1); but none could be obtained from an aliquot portion of (2).

Preliminary studies of the reactions of (1) and (2) with various isocyanates are summarized below:

A- In Absence of Solvent			
Polymer	IPD	MDI	OID
(1)	hard, brown polymer	hard, black polymer	waxy solid
(2)	"	" sticky bl. gum excs. MDI	"
B- In Presence of Solvents			
	IPD	MDI	
(1)	acetone- hard, brown polymer dichloronaphthalene- - - rubbery material diethyl phthalate - - - " "	diethyl- sticky phthalate- black gum	

IPD - Toluene-2,4-diisocyanate

MDI - Methylene-bis-4-phenylisocyanate

OID - Octadecyl isocyanate

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Exhibit C

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Rev. T. A. ToGrodenhuis

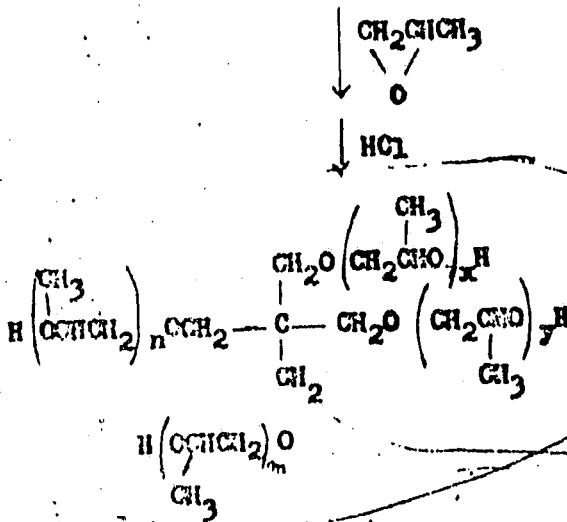
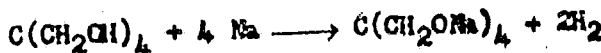
Erna & McCoy  
Brickley Building  
Cleveland, Ohio

Dear Ted:

I am writing to outline our ideas on the possible preparation of vulcanized rubbery polymers from modified polypropylene oxide.

At a rubber conference in Washington last winter, I presented the concept that the polypropylene oxide polymer molecule might have properties particularly suited to a rubber. Since this polymer is normally prepared by a condensation process it would be very difficult to obtain it in a high enough molecular weight to be suitable for the normal type of vulcanization procedures.

Our idea has been to prepare propylene oxide polymers using small amounts of a polyhydric alcohol as the chain starter. Using pentaerythritol we may illustrate as follows:



By varying the ratio of polyhydric alcohol to propylene oxide, the average number of units per each chain can be varied at will. These polymers have been made and are somewhat viscous liquids.

Vulcanization may be accomplished by a process such as esterification with just the proper amount of a dibasic acid such as succinic acid. When such a polymer is heated with succinic anhydride at 170° C. it evolves water, gradually increases in viscosity and gels.

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In cooling this material is soft and rubbery. When a diisocyanate was used as a crosslinker, the material formed a hard, brittle resin on heating.

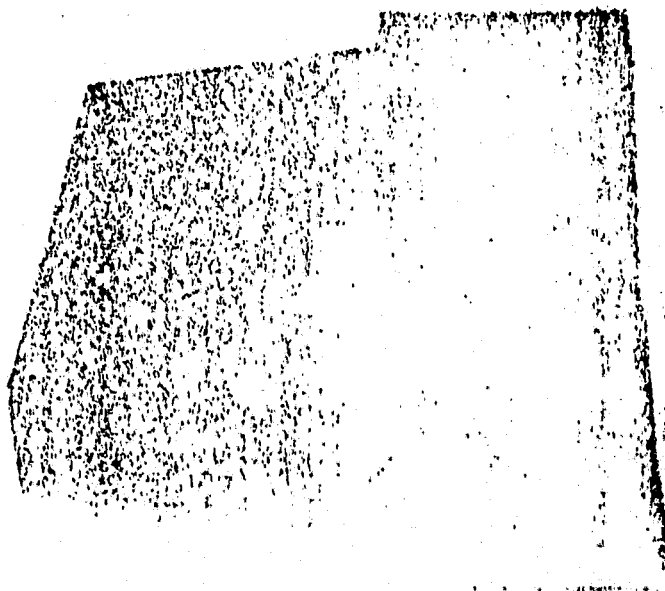
We plan more extensive experiments on the nature of crosslinkers and suitable, the variation in properties with molecular weight, etc. This note is to inform you of the general concept of the work and to request a patent search to see whether we can get fairly broad patent coverage on the idea.

Best regards!

Very truly yours,

*Charlie*  
Charles C. Price

CCP:fm



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Exhibit D

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Progress ReportPropylene Oxide - Pentaerythritol Polymer

AUG 15 1959

DIVISION 60

Summary

- (1) A purified P.O.-P.E.T. polymer of molar ratio 200-to-1 was found to have a molecular weight of 640 as determined cryoscopically.
- (2) P.O.-P.E.T. polymers have been "deionized" by passage through Amberlite exchange resins.
- (3) The reaction between P.O.-P.E.T. polymers and anhydride compounds has been studied more quantitatively. Approximately 3-4 parts by weight of P.O.-P.E.T. polymer react with one part by weight of anhydride compound.
- (4) Details of the preparation of sodium-catalyzed P.O.-P.E.T. polymers of molar ratio of 100-to-1 and 10-to-1 are given. An unidentified by-product, gaseous at room temperature, was found in each case.

(1) Molecular Weight Determination of 200-to-1 Polymer

The cryoscopic method described by Shriner ("Quantitative Organic Analysis", p. 64) was employed using redistilled dioxane as solvent. The data are summarized below: ( $K = 4.7$ )

<u>Wt. of sample (g.)</u>	<u>Wt. of solvent (g.)</u>	<u><math>\Delta T</math></u>	<u>Mol. Wt.</u>
0.064	20.660	0.029	655
0.121	"	0.037	626
			Av. 640

(2) Preparation of "Deionized" P.O.-P.E.T. Polymers

About 1.0 g. of the P.O.-P.E.T. polymer (both 100-to-1 and 10-to-1 were purified in this manner) was dissolved in 30 cc. of redistilled dioxane. This solution was allowed to pass dropwise through a column (1.5 cm. x 8 cm.) packed with Amberlite IR-100-II at atmospheric pressure in about 12 hours. A small portion of the dioxane solution was shaken with distilled water; the aqueous layer was acidic to litmus. The solution was then passed through the column containing Amberlite IR-4B in the course of about 8 hours.

After shaking a small portion of the dioxane solution with water the aqueous

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over was found to be neutral to litmus. The solution was then subjected to steam distillation and that portion distilling up to  $45^{\circ}/5$  mm. was discarded. The residue was used in the reactions with anhydride compounds.

### (3) Reaction Between P.O.-P.E.T. Polymers and Anhydride Compounds

Quantitative studies were made of the reaction between P.O.-P.E.T. polymers and anhydride compounds. The amounts of anhydride compounds which give the best rubbery characteristics are recorded in the following table:

<u>P.O.-P.E.T. Poly.</u>	<u>anhydride Compd.</u>	<u>Reaction Time</u>	<u>Mt. P.O.-P.E.T. St. Anhyd.</u>
crude 100-to-1 16.4010 g.	succinyl chlor. 4.2033 g.	125-130°; 24 hrs. 145-150°; 48 "	3.92
10-to-1 ("deion.") 0.6137 g.	succinyl anhyd. 0.1615 g.	125-130°; 12 " 145-150°; 24 "	3.00
crude 10-to-1 2.8300 g.	succinyl chlor. 1.0379 g.	125-130°; 12 " 145-150°; 24 "	2.72
10-to-1 ("deion.") 4.4253 g.	maleic anhyd. 1.4673 g.	125-130°; 12 " 145-150°; 24 "	3.03

Thus about 3-4 parts by weight of P.O.-P.E.T. polymer reacted with one part by weight of anhydride which is interpreted as meaning there are approximately 4 OH groups per mole of P.O.-P.E.T. polymer, assuming an average molecular weight of about 650.

### (4) Preparation of P.O.-P.E.T. Polymers of Molar Ratio 100-to-1 and 10-to-1

The quantities of reactants used to prepare these polymers are given below:

<u>P.O.-P.E.T.</u>	<u>Sodium (g.)</u>	<u>P.O. (cc.)</u>	<u>P.E.T. (g.)</u>
100-to-1	2.0	70.0	13.6
10-to-1	0.5	"	1.4

These reactions were carried out in a steel pressure bomb. They progressed as follows:

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P.O.-I.E.T. 10-to-1: Yield, 70%

Time (hrs.)	T, (°C.)	Press. (p.s.i.)
0.0	21	atmos.
0.5	99	110
0.8	135	600
1.0	150	420
1.5	154	410
3.5	152	380
14.	143	320
27.	145	315
38.	145	310
48.	147	310
56.	143	290
one week	room	150

P.O.-I.E.T. - 100-to-1: Yield, 75%

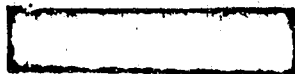
0.0	room	10
0.5	95	50
1.0	120	120
1.3	145	235
1.5	150	200
3.0	158	180
5.0	160	170
10.0	160	150
15.0	163	140
16.0	160	110
25.	160	100
30.	160	100
40.	room	40

In both runs gaseous products at room temperature were formed.

Ralph L. Herbst, Jr.

Charles C. Price

Notre Dame, Indiana



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AUG 15 1956

DIVISION 60

Doc. 7003

DIVISION 60

IN THE UNITED STATES PATENT OFFICE

Applicant: Charles C. Price  
Serial No. 381,999  
Filed September 23, 1953  
For POLYGLYCOL RUBBER

DIV. 50

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Hon. Commissioner of Patents  
Washington 25, D. C.

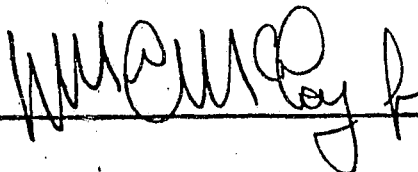
NOTICE OF CHANGE OF FIRM NAME

Sir:

The undersigned, having been appointed attorneys in the above entitled application with full power of substitution and revocation to prosecute this application and to transmit all business in the Patent Office connected therewith, hereby notifies the Office that its firm name has been changed to McCoy, Greene & TeGrotenhuis, Registration No. 12,176, a firm composed of William C. McCoy, Frank S. Greene, Theodore A. TeGrotenhuis and William C. McCoy, Jr., Bulkley Building, Cleveland 15, Ohio.

EVANS & McCOY

By



Cleveland, Ohio

Form 1-54  
Rev. 1-1-54  
THE UNITED STATES OF PATENTS  
WASHINGTON 25, D. C.

DEPARTMENT OF COMMERCE  
UNITED STATES PATENT OFFICE  
WASHINGTON

All communications respecting  
this application should give the  
serial number, date of filing,  
and name of the applicant.

PAPER No. 7

Mr. C. G. Greene & ToProentia  
Polymer Pide.  
Cleveland 11, Ohio

Please find below a communication from the  
EXAMINER in charge of this application.

*Robert C. Clifton*  
Commissioner of Patents.

Applicant		<b>MAILED</b>  MAY 20 1957  PAT. DIV.
Charles G. Price		
Ser. No.	381,999	
Filed	Sept. 23, 1953	
For		
POLYGLYCOL RUBBER		

Responsive to amendment filed August 13, 1956.

1. The claims are 1-6 and 8-12.
2. Claims 1-2, 4-6 and 10-12 are rejected

as not properly defining the alleged invention in:

(A) "until a polymer is formed" (claims 4 and 6) is indefinite since one of the starting materials already is a polymer. (B) Furthermore all of the claims are indefinite in that the nature (i.e. molecular weight) of the product is not specified. Thus the claims include the product of one molecule of the polyalkylene glycol reacted with one molecule of diisocyanate. Such products would not be desirable. (C) Claims 10-12 are indefinite in that the terminal groups of the polyglycol are not specified. (D) Claims 1, 4-6 and 10-12 are unduly broad in not giving proportions of the polyglycol and diisocyanate. All proportions will produce the desired result. Furthermore "parts" in claim 2 is indefinite. Does applicant intend parts by weight, volume, mole, etc? (E) "polyhydric alcohol" (claims 10-12) is unduly broad. The working examples are only pentaerythritol. The term includes the alcohol ether glycol itself. The term also reads

on polyvinyl alcohol or ethylene glycol which are undisclosed. (F) Claims 10 and 12 are indefinite in that the total portion (100%) of the polyglycol polymer is not specified. If ingredients other than the alkylene oxide and the polyhydric alcohol may be included, they should be set forth. (G) "formed from" (claims 4 and 10-12) is indefinite. How is it formed from? (H) "dicarboxylic acid" is too broad. It is not evident that all acids such as acetic acid would produce the desired result. (I) Process claims 4 and 12 are unduly broad in not setting forth the conditions of the reaction, i.e. temperature etc. (J) "alkylene oxide" is unduly broad since applicant has disclosed only ethylene and propylene. (K) claims 1, 4, 5, 11 and 12 present an improper Markush group in the diisocyanates and dicarboxylic acids". The members are so dissimilar in reactivity and type of reaction that it would be repugnant to accepted principles of scientific classification to associate them together as a generic group. Ex parte Burke, 1934 C. D. 5.

3. Claims 1, 2, 4-6 and 10-12 are again rejected as unpatentable over Langerak, Hill or Rupp as set forth in paragraph 3 of the Office action of February 11, 1956. The affidavit under Rule 131 has been considered but is not found to overcome the rejection of record. Exhibit A deals with the reaction of pentaerythritol polyalkylene oxide polymers and also propylene oxide polymers with diisocyanates. The former will not aid in avoiding the rejection on the references since the art is directed solely to the polyalkylene oxide polymers

unmodified by higher functional alcohols. The latter is deficient since no conditions or proportions of the reactions are shown. No specific reaction is set forth. The molecular weight of the propylene oxide polymer is not shown. This deficiency is especially important since it is noted that "hard brittle polymers" were obtained. Applicant at no time, last line of the specification contemplated only rubbery polymers. Furthermore, applicant disclosed no utility for the polymers. Moreover, it is not at all evident that a disclosure solely of propylene oxide polymers and certain of its reaction products with polyhydric alcohols will support claims to any and all polyhydric alcohols, particularly since the reference discloses at least as many species as the propylene oxide polymer species. The affidavit contains no evidence of the generic cover it corresponds in scope to the claims before the effective date of the reference.

4. Claims 1, 4, 5, 11 and 12 are again rejected as unpatentable over DeGroote as set forth in paragraph 5 of the Office action of February 21, 1956. Applicant's affidavits have been considered, and especially Exhibit D, but are not seen to overcome the references. There is no disclosed utility of the polymers in the affidavits.

5. Claims 1, 4, 5, 11 and 12 are also rejected as unpatentable over Boulton as set forth in paragraph 5 of the Office action of February 21, 1956. The polyhydric alcohol in the claims which recite it reads on the polyhydric alcohol itself. Applicant's claims do not define over the reference even if Boulton does not further polymerize the ester produced. However, since the conditions of Boulton's

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operation are not different than applicant's broad process and it may be assumed that the reference likewise produces a printer.

6. Claims 3, 8 and 9 are held to be withdrawn from further consideration under Rule 142 (b) as not readable on the elected species. Claims 1, 2, 4-6 and 10-12 have been rejected. Claim 7 has been cancelled.

DH:ps/p

DH

*B. Mangano*  
Examiner

## IN THE UNITED STATES PATENT OFFICE

Applicant: Charles G. Price  
Serial No: 381,999  
Filed: September 23, 1953  
For: POLYGLYCOL RUBBER

Division 60

A M E N D M E N T

To the Commissioner of Patents:

In response to the Office Action of May 29, 1957,  
please amend the above-identified application, as follows:

In the specification:

Page 10, line 17, cancel "trimethonal" and substitute  
--tri ethylol--;

In the claims:

Cancel claims 1 to 6, inclusive and 8 to 12, inclusive

and enter the following new claims:

1. A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form about 100 parts by weight of a hydroxy terminated polyglycol polymer having a molecular weight of at least 600 and being at least 95 percent formed from units selected from alkylene oxides, at least 20 percent of said units having more than two carbon atoms, further mixing said polyglycol polymer with an polyhydric alcohol having less than 7 carbon atoms and having 3 to 6 primary hydroxyl groups, combining said polyglycol polymer and said polyhydric alcohol with about 1 to 25 parts by weight of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyglycol polymer is formed.

The process of claim 1 in which the reactants are heated from 100 up to 200°C.

15. A process of forming a polyurethane reaction product comprising the steps of mixing (1) about 100 parts by weight of a hydroxy terminated polypropylene ether having a molecular weight of at least 600 with about .01 to 10 mol percent based on the propylene glycol of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 6 hydroxyl groups and (2) about 5 to 25 parts by weight of an organic diisocyanate, and reacting the mixture until a second polymer is formed having residues of said polyhydric alcohol in its molecular chain.

16. A process of preparing a polyurethane reaction product comprising the steps of mixing (1) about 100 parts by weight of a liquid hydroxyl terminated polyglycol polymer having a molecular weight of at least 600 and having a molecular chain comprising alkylene oxide units, at least 90 percent of which is propylene oxide units, with no more than 10 mol percent based on the polymer of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 6 hydroxyl groups, and (2) reacting said polyglycol polymer and said polyhydric alcohol with about 5 to 25 parts by weight of an organic diisocyanate having 2 to 3 functional isocyanate groups to form a reaction product having a chain length substantially greater than that of said polyglycol polymer.

17. A process of preparing a polyurethane reaction product comprising the steps of mixing and reacting (1) about 100 parts by weight of a liquid hydroxyl terminated polyalkylene ether glycol having a molecular weight of at least 500 and having at least 90 mol percent of its molecular chain made of alkylene oxide units having at least 3 carbon atoms, (2) about .01 to 10 mol percent of the glycol of an aliphatic polyhydric alcohol

having 3 to 6 hydroxyl groups so that said polyhydric alcohol becomes part of the main molecular chain of the polyurethane reaction product. and (3) about 5 to 25 parts by weight of an organic polyisocyanate having 2 to 3 functional isocyanate groups for reaction with the hydroxyl terminal groups of the glycol.

18. A product made according to process of claim 13.

19. A product made according to process of claim 14.

20. A product made according to process of claim 16.

21. A product made according to process of claim 17.

22. A process of forming a polyurethane reaction product comprising the steps of mixing (1) about 100 parts by weight of a hydroxy terminated polypropylene ether having a molecular weight of at least 600, with about .01 to 10 mol percent based on the propylene glycol of pentaerythritol and (2) about 5 to 25 parts by weight of an organic diisocyanate, and reacting the mixture until a second polymer is formed.

23. A process of forming a polyurethane comprising the steps of mixing (1) about 100 parts by weight of a hydroxy terminated polypropylene ether having a molecular weight of at least 600, with about .01 to 10 mol percent based on the <sup>of</sup> propylene glycol, trimethylol propane and (2) about 5 to 25 parts by weight of an organic diisocyanate, and reacting the mixture until a second polymer is formed.

24. A polyurethane reaction product of (1) about one mole of an organic diisocyanate and (2) about one mole of a reaction

product of an hydroxy terminated polyalkylene ether glycol having a molecular weight of at least 600 and containing alkylene oxide units of which at least 15 percent are propylene oxide units, and about .01 to 10 mol percent based on the polyalkylene ether glycol of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 4 hydroxyl groups.

#### R E M A R K S

The present invention is directed to a reaction product of a polyalkylene ether glycol which is crosslinked by a coupling agent such as an organic diisocyanate or dicarboxylic acid. In the past it has always been considered desirable to use polymers with relatively long, substantially linear molecular chains in order to make useful articles such as rubber goods. However, in the present invention, polyether glycols with branched molecular chains have been found useful. A novel, unexpectedly useful, high molecular weight reaction product is obtained from relatively short chain polyglycols by modifying them with organic diisocyanates and a small amount of an aliphatic polyhydroxyl material which provides the polyglycol with additional branching and some crosslinking. Instead of the branching and crosslinking action causing the products to be more resinous and hard, the products made with the polyhydroxyl material showed improved abrasion resistance, tensile strength, and flexibility even at low temperature. Some of the unexpected advantages obtained by using the aliphatic polyhydric alcohol may have been due to some crosslinking supplied by the polyhydroxyl material. Instead of the usual urethane linkages, for example, which are formed when the diisocyanate is used as the crosslinking agent.

The claims have been amended to specify the use of a

polyhydric alcohol material. The references cited herein have no disclosure or suggestion that the use of a polyhydric alcohol such as pentaerythritol or trimethylol propane provides reaction products with improved physical properties.

The polyhydric alcohol has been limited by the language "of less than 7 carbon atoms and having from 3 to 6 hydroxyl groups". The polyhydric alcohol is disclosed, for example, on page 2, lines 13 to 15, where a branching operation is described in which a small amount of a tri- or tetra-hydric alcohol is incorporated in the glycol forming material. On page 3, the polyhydric material is described as a polyhydric alcohol having 3 to 6 primary hydroxyl groups. The amount of polyhydric alcohol used in the present invention is specified in the claims as .01 to 10 mol percent of the polyalkylene glycol. The mol percentages are disclosed on pages 2, 3 and 4 of the specification.

Claims 1 to 6 inclusive and 8 to 12 inclusive have been cancelled and new claims 13 to 24 inclusive submitted to point out the invention more clearly. The new claims specify the use of an aliphatic polyhydric alcohol. In claim 22 the use of a particular aliphatic alcohol, namely, pentaerythritol is specified.

Applicant's attorney wishes to thank the Examiner for the interview granted on Sept. 25, 1957. At that time, applicant's attorney indicated that the present application would be restricted to the use of diisocyanates as the coupling agent. During the interview, it was indicated that a reaction between diisocyanate and polyhydric alcohol modified-polyalkylene ether glycols was new.

Also discussed during the interview was the suggestion that the limitation "polyurethane" placed before "reaction product" would probably make the claims more definite. It was

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also suggested that the product claims be drafted by specifying a "product" made according to one of the process claims. Thus, newly submitted claims 17, 18, 19, and 20 are claims of this type.

The comment was made during the interview that the use of organic diisocyanates are preferred over triisocyanates. However, as discussed on page 6, lines 12 to 15, mixtures of organic triisocyanate and diisocyanates may be used. In view of the above disclosure, claims 16 and 17 are submitted which specify the use of an organic polyisocyanate with 2 to 3 functional isocyanate groups.

In response to paragraph 2, part (A), the language "until a polymer is formed" has been deleted and the process step of reacting the mixture until a second polymer is formed has been substituted for the deleted phrase.

In response to parts (B), (C) and (D) of paragraph 2 of the Office Action, the claims have been amended to specify 1 to 25 parts by weight of the coupling agent based on 100 parts by weight of polyglycol. These amounts, as disclosed on page 10 of the specification, are present throughout the claims except for the new claim 24 which calls for about equal molar amounts of the polyalkylene glycol and the organic diisocyanate. The basis for this limitation on the amounts of starting material is found on page 10, lines 26-27.

In response to part (E) of paragraph 2, the polyhydric alcohol has been described generically as a polyhydric alcohol of less than 7 carbon atoms and having from 3 to 6 hydroxyl groups. It is submitted that this is not unduly broad and does not read upon polyalkylene ether glycol, polyvinyl alcohol, or ethylene glycol.

In response to part (F) of paragraph 2, the newly submitted claims have limitations such as "and having hydroxyl end groups" or "hydroxy terminated" to point out the end groups of the polyglycol polymer.

In response to part (G), the language "formed from" has been deleted and the polyglycol polymer described as "having" alkylene units of more than 2 carbon atoms". It is submitted that the claims are now definite.

In response to part (H), claims to the dicarboxylic acid have been dropped in contemplation of a divisional application.

In response to part (I), it is submitted that the process claims are not too broad since the reaction claimed may take place at room temperature even though it is generally too slow to be commercially feasible. The reaction generally is maintained at 75°C. to 150°C. for 10 to 20 minutes or so, as illustrated in the examples.

In response to part (J) applicant has disclosed ethylene oxide, as on page 5, and throughout the specification indicates that alkylene oxides having a larger number of carbon atoms than 2 are desirable for use in the present invention. See for example page 4, where it is stated "propylene oxide units, or other oxide units having at least 3 carbon atoms incorporated in a polymer of sufficiently high molecular weight are required to give the product of the present invention". It is submitted that "alkylene oxide" is not too broad and in view of the above disclosures, and reconsideration of the rejection is requested.

In response to part (K), the Markush group has been cancelled. Rather than to attempt a generic description of the



coupling agent, the application has been restricted to polyisocyanates in accordance with the interview.

In response to the third paragraph of the Office Action, the patent to Langerak shows the preparation of an elastomeric condensation product from (1) polyalkylene ether glycols, (2) arylene diisocyanates, and (3) water under acid conditions and using tertiary organic bases. There is no disclosure or suggestion in Langerak that the polyhydric alcohol of 3 to 6 primary hydroxyl groups can be used to obtain improved reaction products even when relatively short chain polyalkylene ether glycols are used.

The patent to Hill is directed to an elastomeric sponge material formed by (1) a reaction product of a polyalkylene ether glycol and a diisocyanate with (2) from about 100 to 600 parts by weight of water per 100 parts of reaction product.

The patent to Rugg discloses a process for improving scorching properties of elastomers comprising polytetramethylene ether glycol and toluene diisocyanate where chains are extended by reaction with water. The patentee teaches the milling of the polymer at high temperatures to improve the scorching properties of the polymer mixture.

As noted in the patent to Langerak, the Hill and Rugg references have no suggestion of the present invention in which polyalkylene ether glycols are crosslinked with a coupling agent such as an organic diisocyanate with a small amount of a polyhydric alcohol. As noted in paragraph 3, the Examiner also notes the lack of disclosure of a polyhydric alcohol pointing out that the references are directed solely to polyalkylene oxide polymers unmodified by small amounts of highly functional alcohols.

Serial No. 381,999

In response to paragraph 4, the patent to DeGroot shows an xylene soluble reaction product having a molecular weight of 1500 to 15,000 formed by (1) a polycarboxylic acid and (2) a high molal oxypropylene derivative of glucose. A high molal oxypropylene derivative of glucose is not the same as the polyalkylene polymer as specified in the claims of applicant. It is noted that glucose does not have primary hydroxyl groups as does pentaerythritol and trimethylol propane. However, applicant's claims have been amended to specify only organic diisocyanates as the crosslinking agent. The patent to DeGroot does not disclose or teach the use of a polyhydric alcohol which operates even in combination with relatively short chain polyalkylene glycol polymers to produce useful reaction products.

In further response to paragraph 4, applicant is not aware of a law requiring disclosure of utility in the exhibits of Rule 131 affidavits. It is submitted that the disclosure of a rubbery material is enough to fulfill any need for a disclosure.

In regard to the Rule 131 affidavits, it is noted in Exhibit A, second page, lines 8 and 19, the production of rubbery material is disclosed.

In Exhibit B, under the column heading "MDI" in part "A" a sticky black gum is shown. In part "B" of the table, the preparation of a sticky black gum is shown under the column heading "MDI". A rubbery material is also shown under the column heading "IPD" in part "B".

In Exhibit C, page 2, it is recorded that a soft and rubbery material was prepared using succinic acid as a crosslinking agent.

In Exhibit D, under "(3) Reaction Between P.O. - P.E.T. Polymers and Anhydride Compounds", the amounts of anhydride compounds which gave the best rubbery characteristics are recorded. It is also observed in the table that various amounts

of crosslinking agent are shown as being reacted with the polyglycol polymer and polyhydric alcohol.

While applicant submits that his claims distinguish over the references, and that the Rule 131 affidavits are not needed in overcoming the references, he also points out that the Rule 131 Exhibits do show rubbery materials as above described.

In response to the fifth paragraph, the patent to Coulton also has no teaching or disclosure of a polyhydric alcohol, as specified in the claims of the present application. In addition, this reference is directed to reaction of dicarboxylic acid.

The claims now presented are believed to be in condition for allowance and such action is solicited.

Respectfully submitted,

MCCOY, GREENE & TROTSCHNIG  
Attorneys

BY \_\_\_\_\_

Cleveland, Ohio

U. S. DEPARTMENT OF COMMERCE  
PATENT OFFICE  
WASHINGTON

All communications respecting  
this application should give the  
serial number, date of filing,  
and name of the applicant.

PAPER No. 9

McCoy, Greene and  
TeGrotenhuis  
Bulkley Building  
Cleveland 15, Ohio

Applicant: Charles C. Price	
Ser. No. 381,999	
Filed September 23, 1953	
For POLYGLYCOL RUBBER	

Please find below a communication from the  
EXAMINER in charge of this application.

*Robert Chater*

Commissioner of Patents.

16-66457-4 GPO

Responsive to the amendment filed November 21, 1957.

1. The claims are 13-24.

2. Claims 13-24 are again and finally rejected as not properly defining the alleged invention. (A) The claims are broad and indefinite in that the term "polyglycol polymer" as defined implies a mixture of a polyalkylene ether glycol (from the alkylene oxide) and a polyhydric alcohol. Of the specific examples only Example 3 will support these claims and therein it is clear that the "polyglycol polymer" is formed by the condensation reaction of propylene oxide and pentaerythritol. The claims thusly do not define the disclosed invention. Furthermore, this being the sole Example in support of the claims, it is considered that both the "alkylene oxide" and the "polyhydric alcohol" are too broad in view of the use of propylene oxide and pentaerythritol in that example. As a matter of fact applicant discloses his preference for propylene oxide at page 4, lines 14 et seq. of the disclosure. Also polyether glycol polymer would be preferable to "polyglycol polymer".

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(B) The recitation of proportions "by weight" of polyglycol polymer and diisocyanate is not deemed sufficient for the reason that only equimolar proportions or excesses of diisocyanate have been disclosed. This limitation permits an excess of polyglycol (where the molecular weight is low) so that a hydroxyl terminated polyurethane is produced. Such products are beyond applicant's scope and would have doubtful utility. (C) In claim 15 "residues of said polyhydric alcohol" is indefinite. The term does not define what the residue is or how it is connected in the chain. A hydrogen atom is even a residue of the alcohol. (D) In claim 17 the "500" is beyond applicant's scope since only molecular weights of 600 or greater have been disclosed.

3. Claims 13-24 are again and finally rejected as unpatentable over either Langerak, Hill or Rugg as set forth in paragraph 3 of the Office action of May 29, 1957. Applicant's claims are so broad and indefinite as noted in paragraph 2, supra, that no patentable distinction is seen over the reference. The affidavit under Rule 131 filed August 13, 1956 is not considered to aid in overcoming this rejection for the reason that the present claims define a "polyglycol polymer" which is not the same as that disclosed in the affidavit (see paragraph 2 (A), supra). In regard to applicant's contentions that utility is not required in a Rule 131 affidavit, applicant's is referred to the decision *Morway et al. v. Bondi* 1953 C.D. 231. It is furthermore submitted that the mere disclosure of a "rubbery material"

Serial No. 381,999

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is not sufficient utility and in this regard see In re  
Brenner 1950 C.D. 342.

4. Claims 13-24, all the claims in the case,  
have been rejected.

5. This rejection is made FINAL.

DAHoes/sss

*Dast.*

*C. Mangan*  
Examiner

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Doc. 7003

RECEIVED

IN THE UNITED STATES PATENT OFFICE

JUL 21 1954

DIVISION 60

Applicant: Charles C. Price

Serial No: 381,999  
Filed: September 23, 1953  
For: POLYGLYCOL RUBBER

Division 60

AMENDMENT AFTER FINAL REJECTION

To the Commissioner of Patents:

In response to the Office Action of December 20, 1957, please amend the above-identified application, as follows:

In the claims:

Claim 13, lines 2 and 3, after "form" delete "about 100 parts by weight of"; line 3, after "terminated" delete "polyglycol" and substitute --polyether glycol--; line 4, after "600" delete "and being at least 95 percent formed from units selected from alkylene oxides, at least 20 percent of said units having more than two carbon atoms, further mixing said polyglycol polymer with an" and substitute --which is a condensation product of an alkylene oxide having from 2 to 4 carbon atoms and a--; line 8, after "groups" insert --, at least 20 percent of said alkylene oxide having more than 2 carbon atoms--; line 9, after "said" delete "polyglycol" and substitute --polyether glycol--; same line, after "polymer" delete "and said polyhydric alcohol"; line 10, delete "about 5 to 25 parts by weight" and substitute --at least about an equal molar amount--; same line after "diisocyanate" insert --based on said polyglycol polymer--; line 12, after "said" delete "polyglycol" and substitute --polyether glycol--.

Claim 14, line 1, after "claim" delete "16" and substitute --13--.

Claim 15, line 2, after "(1)" delete "about 100 parts by weight of a hydroxy terminated polypropylene ether having a molecular weight of at least 600 with" and substitute --a condensation product of propylene oxide and--; line 5, after "propylene" delete "glycol" and substitute --oxide--; line 6, after "groups" insert --, said condensation product having a molecular weight of at least 600--; line 7, after "(2)" delete "about 5 to 25 parts by weight" and substitute --at least about one mole per mol of condensation product--; line 8, after "formed" delete balance of claim and substitute --period (.)--.

Claim 16, line 2, after (1) delete "about 100 parts by weight of"; lines 3 and 4, after "terminated" delete "polyglycol polymer having a molecular weight of at least 600 and having a molecular chain comprising alkylene oxide units, at least 90 percent of which is propylene oxide units, with" and substitute --condensation product of propylene oxide and--; line 7, after "the" delete "polymer" and substitute --propylene oxide--; line 9, after "said" delete "polyglycol polymer and said polyhydric alcohol" and substitute --condensation product--; same line, after "with" delete "about" and insert --at least--; line 10, delete "5 to 25 parts by weight" and substitute --equal molar amounts based on said condensation product--; same line, after "organic" delete "diisocyanate" and substitute --polyisocyanate--; line 12, after "said" delete "polyglycol polymer" and substitute --condensation product.

Claim 17, lines 2 and 3, after "(1)", delete "about 100 parts by weight"; lines 3 and 4, after "terminated" delete "polyalkylene ether glycol having a molecular weight of at least 500 and having at least 90 mol percent of its molecular chain made of" and substitute --condensation product of an--; line 6,



after "oxide" delete "units"; line 6, after "comma (,)", delete "(2)" and substitute --and--; line 7, after "the" delete "glycol" and substitute --alkylene oxide--; lines 8, 9 and 10, after "groups" delete "so that said polyhydric alcohol becomes part of the main molecular chain of the polyurethane reaction product" and substitute --, said condensation product having a molecular weight of at least 600--; line 10, after "and" delete "(3) about 5 to 25 parts by weight" and substitute --(2) an excess--; line 12 after "groups" insert --over that required--; line 13, delete "glycol" and substitute --condensation product--.

Claim 22, line 2, after (1) insert --a first polymer comprising a condensation product of--; line 3, after "a" delete "hydroxy terminated polypropylene ether having a molecular weight of at least 600," and substitute --propylene oxide--; line 4, delete "with" and substitute --and--; line 5, after "propylene" delete "glycol" and substitute --oxide--; lines 5 and 6, after "(2)" delete "about 5 to 25 parts by weight" and substitute --at least about an equal molar amount based on the amount of said condensation product used--.

Claim 23, line 2, after (1) insert --a condensation product of propylene oxide and--; same line, delete "about 100 parts by weight of a hydroxy terminated polypropylene ether having a molecular weight of at least 600 with"; line 5, after (2) delete "about 5 to 25 parts by weight" and substitute --at least about an equal molar amount based on the amount of said condensation product used--; line 7, after "a" delete "second polymer" and substitute --polyurethane--.

Claim 24, line 2, after "a" delete "reaction" and substitute --condensation--; line 3 after "of" delete "an hydroxy terminated polyalkylene ether glycol having a molecular weight of

at least 600 and containing alkylene oxide units" and substitute --an alkylene oxide of 2 to 4 carbon atoms--; line 6, after "oxido", delete "units"; line 7, delete "polyalkylene ether glycol" and substitute --alkylene oxide--; line 8, delete "period (.)" and insert --, said condensation product being hydroxy terminated and having a molecular weight of at least 600.---

#### R E M A R K S

The claims have been amended to overcome the objections of the Examiner. In the claim 13 the term "polyglycol" has been changed to --polyether glycol-- as suggested by the Examiner to more clearly define the starting polyglycol polymer.

The claims have been amended to more clearly point out the invention and particularly to define the polyglycol polymer as a condensation product of an alkylene oxide and a polyhydric alcohol. In claim 13, for example the polyether glycol polymer is specified as a condensation product of an alkylene oxide having 2 to 4 carbon atoms and a polyhydric alcohol. It is also specified that at least 20 percent of the alkylene oxide be an alkylene oxide having more than 2 carbon atoms. The above limitations are supported by the specification which points out that ethylene oxide, propylene oxide and butylene oxide may be used as discussed later in more detail.

In claim 15 the polyether glycol polymer is defined as a condensation product of propylene oxide and a polyhydric alcohol. Claims 22 and 23 are limited to condensation products of propylene oxide with pentaerythritol and trimethylolpropane respectively.

The above limitations should satisfy the Examiner's criticisms in both paragraphs 2 and 3 that the claims were broad and indefinite.

Also in response to paragraph 2A of the Office Action of December 20, 1957, it is submitted that the terms "alkylene oxide" and "polyhydric alcohol" are not too broad in view of the fact that only propylene oxide and pentaerythritol are shown in Example 3. Other specific materials are disclosed in the specification so that anyone skilled in the art could reproduce the invention defined in applicant's claims. For example, claim 13 as now amended, calls for an alkylene oxide of 2 to 4 carbon atoms and further limits the alkylene oxide to at least 20 percent propylene oxide. Alkylene oxides of 2, 3 and 4 carbon atoms are disclosed on pages 4 and 5 of the specification. A basis for the limitation of 20 percent propylene oxide is found on page 5, lines 1 and 8.

As discussed in the amendment of November 21, 1957, the polyhydric alcohol and the amounts of polyhydric alcohol used are disclosed on pages 2, 3 and 4 of the specification.

It is again submitted that one skilled in the art, reading the specification and following the working example, could practice the present invention.

In response to part B of paragraph 2, the claims have been amended to specify that the proportions of polyisocyanate to polyether glycol polymer be at least equimolar amounts. Some of the claims call for excess polyisocyanate and specify the use of excess polyisocyanate over that required to react with the hydroxyl end groups of the polyether glycol polymer. Even though applicant has disclosed the proportions on the weight basis, the proportions by weight have been deleted from the claims and the amounts expressed on a molar basis as suggested by the Examiner.

In response to part C of paragraph 2, the term "residues" of a polyhydric alcohol has been deleted from claim 15.

In response to part D of paragraph 2, the molecular weight of "500" has been changed to "600" as suggested by the Examiner.

In response to paragraph 3, it is submitted that the claims as now presented are not so broad and indefinite that they do not distinguish over the references. As pointed out in the amendment of November 21, 1957, there is no suggestion of the use of a condensation product of an alkylene oxide and a polyhydric alcohol in Langerak, Rugg or Hill. The condensation products of alkylene oxides and polyhydric alcohols, in which the polyhydric alcohols are used as chain starters for the polyether glycol polymer, are not disclosed in the above patents.

Also in response to paragraph 3, it is submitted that the claims define a polyether glycol polymer that is disclosed in the Rule 131 affidavit, although it is again contended that the Rule 131 affidavit is not needed since the claims distinguish from the references.

In regard to utility requirements of Rule 131 exhibits, the Morway et al vs. Bondi (1953 C.D. 231) case is directed to an interference between two parties. One of the parties attempted to show reduction to practice of a lubricant by showing a mixing of ingredients to form a lubricant composition. The mixing was held not to be enough to establish reduction to practice in that particular case, because production of a certain type of heavy dirty grease was not shown by mere mixing in contrast to presenting tests that would show the grease possessed the properties desired.

It is submitted the Morway et al case is not controlling in the present case. Even on page 235 of the Morway et al case it is recognized that products may be reduced to practice when made and without further testing. A portion of page 235 is quoted as follows:

"Certain products or substances may be held fully reduced to practice when made, without the need of tests, because the utility in the pertinent art is well understood. Larson et al v. Eicher"

The In re Brenner (1950 C.D. 342) case does not hold that mere disclosure of a rubbery material in a Rule 131 exhibit is insufficient to disclose utility. There is no mention of a Rule 131 affidavit in the case, the case being directed to the requirement for utility in an application. Even if utility were required in a Rule 131 exhibit, disclosure of a "rubbery" material in the present case is an indication of the use or uses intended which would be enough to show utility in an application according to the In re Brenner case.

It is submitted that the claims are now in condition for allowance and such allowance is solicited.

Respectfully submitted,

McCOY, GREENE & TEGROTENHUIS  
Attorneys

Cleveland, Ohio

BY *James E. McGrotenhuis*

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ADDRESS ONLY  
THE COMMISSIONER OF PATENTS  
WASHINGTON 25, D. C.

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U. S. DEPARTMENT OF COMMERCE  
PATENT OFFICE  
WASHINGTON

All communications respecting  
this application should give the  
serial number, date of filing,  
and name of the applicant.

PAPER No. 11

McGoy, Green and McCrotenhuis  
with their attorneys  
c/o Howard 15, 1958

Please find below a communication from the  
EXAMINER in charge of this application.

*Robert C. Watson*

Commissioner of Patents.

Applicant: Charles C. Price	
Ser. No. 381,900	MAR 13 1958 DIV
Filed Sept. 23, 1953	
For POLYGLYCOL RUBBER	

18-00457-4 GPO

Responsive to the amendment filed February 19, 1958.

1. The proposed amendment filed February 19, 1958  
has not been entered as it fails to place the case in  
condition for allowance.

2. If the proposed amendment were entered,  
the claims in the case would still be 13-24. In view  
of the numerous cancellations and amendments in the proposed  
amendment, a clear copy of the claims must be supplied  
if any further amendments are proposed.

3. Claims 13-24 would still be considered  
unacceptable for the reason that they fail to particularly  
point out and distinctly claim the alleged invention. While  
the proposed amendment appears to correct most of the  
objections noted in paragraph/2 of the Final Rejection,  
the following objections still appear. In claim 13  
the word "tripe" could now be unnecessarily repeated.  
Also in the third to the last line of the amendment  
to that claim "polyglycol" is inaccurate and should be  
replaced by "polyether glycol". In claim 15 there is  
no indication of the molecular weight of the

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resultant polyurethane. In claim 16 the phrase "no more than 10 mole percent --- of an --- alcohol" includes zero percent which applicant has expressly desired to exclude. In claim 17 the "of" of line 3 should now be deleted. Also in claim 17, line 7 "of the glycol" is unnecessary and makes for indefiniteness. In claim 22 there is no indication of the molecular weight of the polyether glycol. In claim 23 the comma in line 4 after "600" should also be deleted. Also in claim 23 there is no indication of the molecular weight of the polyether glycol. Furthermore, in claim 24, line 5, the "are" should be replaced by "is". In <sup>in</sup> claims 15, 17, 22, 23 and 24 applicant should recite/a positive manner that a polyurethane reaction product is obtained. The language of claims 13 and 16 is adequate in this regard; namely, that "reacting the mixture until a second polymer having a chain length greater than that of said polyether glycol polymer is formed." As these claims stand the "second polymer" is not critically different than the polyether glycol.

4. Claim 16 would still be considered unpatentable over either Langerak, Hill or Rugg as set forth in paragraph 3 of the Final Rejection. Since as pointed out in paragraph 3 of the instant Office action this claim does not require the alcohol to be present, it does therefore not avoid the references. Again the affidavit under Rule 131 is unacceptable for the reason that no utility is shown therein. Even the disclosure of the use of a polymer as a "film" is insufficient utility. Partracarbon Limited v. Robert C. Watson, Commissioner of Patents, 724 O.G. 432.

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5. If the proposed amendment were entered,  
paras 13 to 20 would still be finally rejected.

6. Applicant is advised that a proper response  
to the Final Rejection must be made within the 6 month  
statutory period running from the date of the said  
Final Rejection.

7. The proposed amendment will be entered  
for purposes of appeal if applicant so indicates upon  
filing of his Notice of Appeal and Brief.

cc: 1005:SSS

W.A.H.

*C. J. Morgan*  
Examiner



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Doc. 7003

IN THE UNITED STATES PATENT OFFICE

Applicant: Charles C. Price  
Serial No: 381,999  
Filed: September 23, 1953  
For: POLYGLYCOL RUBBER

Pat. Div. 60 (1)

AMENDMENT AFTER FINAL REJECTION

To the Commissioner of Patents:

In response to the Office Action of December 20, 1957 and March 13, 1958, please amend the above-entitled application, as follows:

In the claims:

Rewrite claims 13-24 as follows:

25. A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) a hydroxy terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide having from 2 to 4 carbon atoms and a polyhydric alcohol having less than 7 carbon atoms and having 3 to 6 primary hydroxyl groups, at least 20 percent of said alkylene oxide having more than 2 carbon atoms, and (2) at least about an equal molar amount of an organic diisocyanate based on said polyether glycol, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether glycol polymer is formed.

26. The process of claim 25 in which the reactants are heated from 100 up to 200°C.

27. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of

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propylene oxide and about .01 to 10 mol percent based on the propylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 6 hydroxyl groups, said condensation product having a molecular weight of at least 600 and (2) at least about one mole per mol of condensation product of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

28. A process of preparing a polyurethane reaction product comprising the steps of mixing (1) a liquid hydroxyl terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of propylene oxide and about .01 to 10 mol percent based on the propylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 6 hydroxyl groups and (2) at least an equal molar amount based on said condensation product of an organic polyisocyanate having 2 to 3 functional isocyanate groups, and reacting the mixture to form a reaction product having a chain length substantially greater than that of said polyether glycol polymer.

29. A process of preparing a polyurethane reaction product comprising the steps of mixing (1) a liquid hydroxyl terminated condensation product of an alkylene oxide having at least 3 carbon atoms, and about .01 to 10 mol percent based on the alkylene oxide of an aliphatic polyhydric alcohol having 3 to 6 hydroxyl groups, said condensation product having a molecular weight of at least 600, and (2) an excess of an organic polyisocyanate having 2 to 3 functional isocyanate groups over that required for reaction with the hydroxyl terminal groups of the condensation product, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

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30. A product made according to process of claim 25.
31. A product made according to process of claim 26.
32. A product made according to process of claim 28.
33. A product made according to process of claim 29.
34. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a first polymer comprising a condensation product of about 100 parts by weight of propylene oxide and about .01 to 10 mol percent based on the propylene oxide of pentaerythritol, said first polymer having a molecular weight of at least 600, and (2) at least about an equal molar amount based on the amount of said condensation product used of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said first polymer is formed.
35. A process of forming a polyurethane comprising the steps of mixing (1) a condensation product of propylene oxide and about .01 to 10 mol percent based on the propylene oxide of trimethylol propane, said condensation product having a molecular weight of at least 600, and (2) at least about an equal molar amount based on the amount of said condensation product used of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.
36. A polyurethane reaction product of (1) about one mole of an organic diisocyanate and (2) about one mole of a condensation product of an alkylene oxide of 2 to 4 carbon atoms of which at least 15 percent is propylene oxide, and about .01 to 10 mol percent based on the alkylene oxide of an aliphatic

polyhydric alcohol of less than 7 carbon atoms and having 3 to 4 hydroxyl groups, said condensation product being hydroxy terminated and having a molecular weight of at least 600, said polyurethane reaction product having a chain length substantially greater than that of said condensation product.

R E M A R K S

In response to the Office Action of December 20, 1957, and March 13, 1958, please disregard the amendment filed February 19, 1958 and enter the present amendment in which claims 13 to 24 have been rewritten as claims 25-36 respectively to provide clean copy.

In addition, changes have been made in claims to correct the objections expressed in paragraph 3 of the Office Action of March 13, 1958.

In particular response to paragraph 3, claim 25 (old claim 13) is submitted in which the word "mixing" is not repeated as it was in line 9 of old claim 13. Also the "polyglycol" in the third to last line of amendment to claim 13 has been replaced by --polyether glycol--. Applicant's attorney wishes to thank the Examiner for pointing out these errors and omissions.

Claim 15 has been rewritten as claim 27. The molecular weight of the resultant polyurethane has been indicated by the language "reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed." In a similar manner, limitations have been included in claims 27, 29, 34, 35 and 36 (old claims 15, 17, 22, 23 and 24) to recite in a positive manner that a polyurethane reaction product is obtained.

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Now claim 28 (old claim 16) now specifies that about .01 to 10 mol percent of a polyhydric alcohol be used which excludes zero percent.

The word "of" in line 3 of claim 17 (now rewritten as claim 29) has been deleted. Also the words "of the glycol" formerly appearing in line 7 of claim 17 have been substituted for by the words --based on the alkylene oxide--.

In claim 34 (formerly claim 22) the molecular weight of the polyether glycol polymer has been specified as 600 by the following language inserted in line 5 of claim 22 after "pentaerythritol"

"--said first polymer having a molecular weight of at least 600--"

In claim 23 (now claim 35) the deletion of the comma (,) in line 4 after "600" was inadvertently omitted from the proposed amendment of February 19, 1958. This has been taken care of in the rewritten claim 35. Also in claim 35, the molecular weight of the condensation product is specified as at least 600.

In claim 24 (now claim 36) the word "are" in line 5 has been replaced by --is--.

In response to paragraph 4 of the Office Action of March 13, 1958, claim 16 (now claim 28) has been rewritten as indicated above to specify the use of .01 to 10 mol percent of the polyhydric alcohol in place of the language "no more than 10 mol percent." The lower portion of the polyhydric alcohol name had been previously omitted in claim 16. Claim 28 (rewritten from claim 16) now distinguishes from the references cited in paragraph 3 of the Final Rejection.

While the Rule 131 affidavit is not needed to overcome the reference, it is noted that the Petrocarbon Ltd. case

Ser. No. 281,999

(72d O.G. 432, 114 U.S.P.Q. 95) is directed to a requirement for utility in an application and makes no reference to a Rule 131 exhibit.

Applicant has made an earnest effort to prepare the claims for allowance and appreciates the errors and omissions kindly pointed out by the Examiner. It is submitted that all claims are now in condition for allowance and such allowance is solicited.

Respectfully submitted,

McCOY, GREENE & TOGROTENHUIS  
Attorneys

BY 

Cleveland, Ohio

DEFENDANT'S EXHIBIT E

Letter dated September 11, 1961

From: T. TeGrotenhuis

To: C. Price

Page 905a

905a

McCOY, GREENE & TEGROTENHUIS

WILLIAM C. MCCOY  
FRANK S. GREENE  
T. A. TEGROTENHUIS  
WILLIAM C. MCCOY, JR.  
VINCENT A. GREENE  
DENISON B. MATTHEWS  
RICHARD M. HOWELL

BULKLEY BUILDING  
CLEVELAND 15, OHIO

PATENT AND  
TRADEMARK  
LAWYERS  
MAIN 1-0470

September 11, 1961

Dr. Charles C. Price  
John Harrison Laboratory of Chemistry  
University of Pennsylvania  
Philadelphia 4, Pennsylvania

218

Re: 7003-Intf. - Price Vs. Heiss, Intf. No.  
90,414

Dear Charlie:

I'm glad you liked my brief in your interference, however, the date it was received, we got a postponement of the hearing to February 1st. In response to this, I filed a petition to the Commissioner of Patents and I also called Hoarce B. Fay, Jr., the Assistant Commissioner, who is a very good friend of mine and for whom I have done many favors. On September 7th, however, I received a reply by the Senior Party Heiss to reschedule the final hearing for a day in November. I am enclosing herewith a copy of our petition and also the reply.

I am extremely confident of winning this case on the first grounds. The only reason I argued to any extent on the reduction of practice at Notre Dame was to prevent others in the future from immediately considering the Windemuth application of Bayer as prior art to yours. The work done at Notre Dame would never win the interference for a Junior Party, but I am certain that the Board, or the Court, at least, will never decide the interference on the ground that Heiss cannot make the counts. As you remember, in only the very first couple of experiments performed did Herbst use diisocyanates. All the others used dicarboxylic acids or anhydrides. You can expect Flick to make the most of the argument against the reduction of practice, but I am confident he will lose the interference. In other words, I think you can rely pretty strongly on collecting your share of the \$1,000,000 royalty.

Very truly yours,

*T. A. TeGrotenhuis*  
T. A. TeGrotenhuis

TAT:jf



DEFENDANT'S EXHIBIT I

Certified copy Motion to Dissolve, dated March 31, 1960,  
Interference No. 90,414

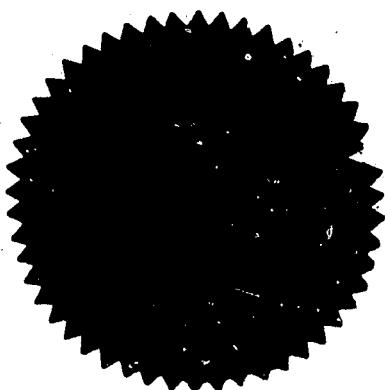
Pages 906a to 918a

PO-55-Rev  
(6-16-61)

906a

U. S. DEPARTMENT OF COMMERCE  
UNITED STATES PATENT OFFICEJanuary 4, 1973  
(Date)

THIS IS TO CERTIFY that the annexed is a true copy from the records of this office of Certain Requested Documents, filed March 31, 1960, in Interference Number 90,414.



By authority of the  
COMMISSIONER OF PATENTS

*W. B. Zwalden*

Certifying Officer.

Doc

IN THE UNITED STATES PATENT OFFICE  
BEFORE THE BOARD OF PATENT INTERFERENCES

CHARLES C. PRICE

vs.

Intf. No. 90414

HERBERT L. HEISS

To the Commissioner of Patents:

MOTION TO DISSOLVE

The party Charles C. Price moves under the provisions of Rule 232 that this interference be dissolved on the following grounds:

- (a) The Party Heiss has no right to make the claims forming the counts of the interference.
- (b) The claims forming the counts of the interference are not patentable to the Party Heiss while being patentable to the Party Price.

Argument Relative to Ground (a) Above

As will be seen from the Price patent in interference, each of the counts specifies that the hydroxy terminated polyethyl glycol polymer has a molecular weight of at least 600. As will be seen from a study of the file history and also a study of the patent, this "600" limitation is critical. The Heiss application contains no disclosure whatsoever of a condensation product of an alcohol having more than two hydroxyl groups with propylene oxide or with any alkylene oxide having three or more carbon atoms and having a molecular weight of at least 600.

In arguing with the Examiner concerning his right to make the counts, the party Heiss misled the Examiner by insisting that the molecular weight of the condensation product of 13.2 mols of propylene oxide with 1 mol of glycerin necessarily or inherently has a molecular weight of at least 600. He based his argument on the fact that 13.2 times the molecular

DOCKET DIVISION

COMM. FILE

weight of propylene oxide, plus the molecular weight of glycerin is more than 600. It will be shown herein that while there is no dispute as to the arithmetic of the Party Heiss, there is no basis in fact for any assumption that the molecular weight of the condensation product will be anywhere near 600 molecular weight.

In his action of October 2, 1958, the Examiner in paragraph 5 pointed out to the Party Heiss that the conditions of reaction, temperature, catalyst and molecular weight of the alkylene oxide-organic trihydroxy compound is not set forth in the specification and that applicant Heiss was merely extending an invitation to the public to experiment and determine what molecular weight is most desirable. The Party Heiss pointed out in his answer to the Examiner that the condensation of glycerol and propylene oxide is old in the art as described in Schmidt Patent 1,922,459, Melvin DeGroote et al patent 2,357,933 and Melvin DeGroote et al patent 2,357,937, falsely indicating that the product of the specification was a product necessarily made under these patents. There is nothing in the application of Heiss as filed to indicate how the product was made or under what patent it would have been made, and even if it was made under any of these patents, which certainly cannot be presumed that it would have a molecular weight of at least 600. However, Party Heiss by reference to these patents in an attempt to supply an essential part of his disclosure certainly must recognize the data and authority of Melvin DeGroote in this field of condensation products. He in fact referred to these patentees

"as evidence that skilled artisans could make applicant's condensation product"  
(page 11 of amendment and filed February 6, 1959).

It will be hereinafter shown that publications of Mr. DeGroote show the molecular weight to be only a fraction of the value as calculated by Party Heiss.

Party Price contends, and it will be shown herein by reference to printed literature, that it is recognized that

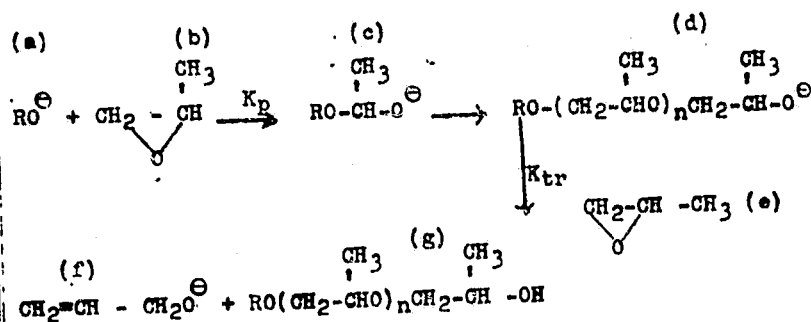
the molecular weight of a condensation product of propylene oxide and an initiator is not that computed in the manner of Heiss but is only a fraction of this computed value, which would be the maximum molecular weight theoretically possible if there were no other reactions but growth on the alcoholic hydroxyl of the glycerol.

The molecular weight of a product obtained from a mixture of 1 mol of glycerol and 13.2 mols of propylene oxide may in fact vary all over the lot, depending on the process used and reaction conditions, and a molecular weight of 600 is not inherently obtained. The maximum possible theoretical molecular weight of a condensation product of 13.2 mols of propylene oxide and 1 mol of glycerin would be, as Party Heiss contends, around 800+ if all the propylene oxide became connected to a glycerol residue. However, there are several factors that influence the molecular weight of the product obtained, as follows:

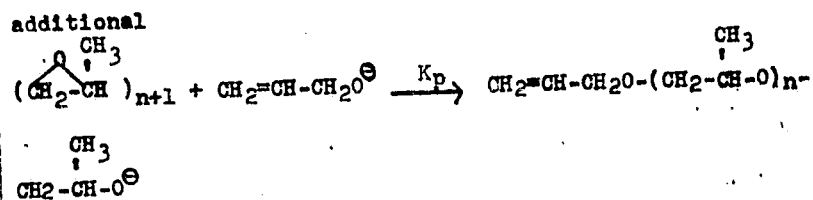
First, glycerol is readily and usually adventitiously contaminated with other initiators. It is well known for its ability to absorb moisture and most commercial glycerol contains an appreciable water content. If one makes the reasonable assumption that the glycerol Heiss used contained 10% water (weight basis) and that water and glycerol are equally effective initiators, then the molecular weight even without any chain transfer would be less than 500.

Second, under many polymerization conditions, the molecular weight of a condensation product of any hydroxy compound and propylene oxide is determined far more by ratio of propagation to transfer  $K_p/K_{tr}$  than by ratio of monomer to initiator  $([M] / [I])$ .

The sequence of reactions involved in the polymerization of propylene oxide on any initiator  $RO^\ominus$  is as follows, where  $K_p$  is the propagation coefficient and  $K_{tr}$  is the transfer coefficient.



then (f) acts as initiator with propylene oxide as follows:



It is seen from the above that new initiators are formed by chain transfer, a process well known to all polymer chemists. These new initiators act just as did the original initiator present and therefore reduce the amount of propylene oxide available for growth on glycerol and thus greatly reduce the molecular weight from the value as computed by Party Heiss. Even the allyl ether end groups in the presence of base, readily rearrange to propenyl end groups susceptible to hydrolysis in polymer purification by a dilute acid wash, so the molecular weight obtained is still lower.

DeGroot, Recognized By Party Heiss As Being Skilled Artisan, Shows That Calculated Molecular Weight and Actual Molecular Weight of Glycerol Propylene Oxide Condensation Products Are Very Different

The Party Heiss on page 11 of the amendment filed February 6, 1959 referred to certain DeGroot Patents, Nos. 2,357,933 to 2,357,937, inclusive, as evidence that "the skilled artisan could make applicants' condensation product..". This same skilled artisan shows in Patent 2,609,932 that the

condensation product of glycerol and propylene oxide is only a fraction of what one would expect if calculations were made upon the basis used by the Party Heiss. Thus, referring to Table 1, columns 9 and 10, it is seen that where the theoretical molecular weight was 10,900, the actual molecular weight was but 4,275, where the theoretical molecular weight is 9665, the actual molecular weight was 3910; where the theoretical molecular weight was 7765, the actual molecular weight was 3760; etc. The only conclusion that can be drawn from this patent is that certainly by the method of making condensation products as shown by DeGroot, the calculations of theoretical molecular weight are of no value.

DeGroot Patent 2,771,471, points out in column 4, lines 10 et seq,

"Oxypropylations are conducted under a wide variety of conditions, not only in regard to presence or absence of catalyst, and the kind of catalyst, but also in regard to the time of reaction, temperature of reaction, speed of reaction, pressure during reaction, etc."

The entire columns 4, 5 and 6 of this DeGroot patent point out differences obtained under different condensation conditions. The reaction can take place even with explosive violence under some conditions and it is impossible to have the same molecular weight obtained under all conditions. In Table 1, columns 7 and 8, it will be seen again that the theoretical molecular weight, which is calculated on the basis proposed by Heiss may be several times the actual molecular weight. There is in fact no definite relation between calculated or theoretical molecular weight and the molecular weight actually obtained.

#### Other Patents Confirm DeGroot

The Lundsted Patent 2,674,619, which is assigned to Wyandotte Chemicals Corporation of Wyandotte, Michigan, shows

For example in Example 1 that whereas a molecular weight of propylene oxide initiated by propylene glycol was calculated as 2380 on the basis used by Party Heiss the final product as measured had a molecular weight of only 1620. Column 6, lines 1-4, the patentee states,

"It will be noted in Part A of the above example that the molecular weight, as determined by hydroxyl number, was appreciably lower than the calculated molecular weight."

The Sokol Patent 2,527,970, which is assigned to Heyden Chemical Corporation, states (col. 2, lines 15 et seq),

"When certain catalysts are used the product is a mixture of the expected pentaerythritol hydroxy ether and varying amounts of polymers of ethylene oxide."

After referring to the condensation of pentaerythritol and propylene oxide which should have produced a m. w. of 830, Sokol says:

"However, the molecular weight of the mixed product is much lower than would correspond to such a compound." (lines 38-40 col. 2)

Sokol also points out, column 3, lines 43-46,

"I have found that small but significant amounts of water favor the polymerization of the alkene oxide and hinder or suppress the desired reaction of the alkene oxide with the polyhydric alcohol."

This shows, as previously stated, that any absorbed moisture in the glycerin must be considered and also greatly reduces molecular weight obtained. In the table appearing across columns 5 and 6 of the patent, Sokol points out that when utilizing the particular catalysts there described, a molecular weight of 650 should have been obtained on the basis of calculation, a molecular weight of only 328 was obtained, and when the molecular weight should have been 782 on the basis of calculation such as



made by Heiss the molecular weight was only 291 when measured. In every case, as shown by comparison of the last two columns of this table, the molecular weight is but a fraction of that theoretically obtained. It is obvious therefore that molecular weight depends upon conditions of the reaction and the particular catalyst used.

Doctor's Thesis in Notre Dame Library Also  
Shows Fallacy of Heiss' Computations

Applicant is enclosing herewith a photostat of pages 11 to 15, inclusive of Dr. St. Pierre's thesis which appears in the Library of Notre Dame University and is available to all people desiring it. This thesis, which is dated 22nd July, 1954, clearly shows that where one would expect by calculation a value of over 16000 molecular weight, there is actually obtained a molecular weight of only 794, which is but a fraction of the calculated or theoretical value. The bound library copy of which will be handed to the Examiner and will be available at the hearing for inspection.

In each polymerization of Dr. St. Pierre, it is pointed out that the initiator is a fraction of the material of the previous reaction. He started with .015 mols of initiator sodium methoxide in Example 1 and produced about 44 grams of product. 20 grams of this containing about  $\frac{1}{2}$  of the .015 moles of original initiator was used for Example 2 or .007 moles of initiator.  $\frac{25}{50}$  of the product of Example 2 containing  $\frac{5}{12} \times .007$  = .003 moles of original initiator was used for Example 3 etc. The total propylene oxide in Example 2 was  $20 \times \frac{44}{100} \times .75$  mole + .69 mole = about 1 mole. The propylene oxide in Example 3 was  $\frac{25}{50} \times 1$  mole + .69 moles = about 1.2 moles. This corresponds to over 300 moles of propylene oxide to one mole of initiator. The m.w. computed on such a basis should have been over 16,000

whereas the measured value as shown on page 14 was only 794. Dr. St. Pierre's thesis also shows, therefore, that the molecular weight calculated on the basis of initiator initially present is not obtained and that the molecular weight obtained in the product is determined by the particular process by which the polymer is formed, and the conditions of the reaction which determine the relative rate of polymer propagation and chain transfer, as illustrated above.

Heiss Does Not Disclose Process by Which Condensation Product is Made

Attorneys of Party Price have thoroughly studied the application of Party Heiss and have been unable to find anywhere in this application, as filed, any statement as to how condensation products are made, or any statement as to their molecular weights. It is therefore seen, in view of the art herein cited and particularly that of DeGroot, who the Party Heiss first recognized as being a "skilled artisan" in the field and who was first relied upon by the Party Heiss, that the molecular weight cannot be properly calculated on the basis of the assumption that all of the propylene oxide grows on the alcohol initiators, i.e., in this case the hydroxyl groups of glycerin.

Reason Also Shows Heiss Different

That the molecular weight cannot be determined by calculation on the basis used by Party Heiss is also illustrated by the fact that if the proportion of glycerin was only one in a thousand, the molecular weight of the condensation product according to Party Heiss would have to be 1000 times the molecular weight of propylene oxide, which is 57 plus the molecular weight of glycerin, or 57,093. If the amount of propylene oxide were reduced to 1 part in a million, the molecular weight would have to be 57,000,093; if the amount of glycerin was reduced to zero,

the molecular weight according to Party Heiss' calculation would necessarily be infinite, which obviously would never occur.

It is submitted that the only possible conclusion from the above is that the molecular weight of the condensation product of 13.2 mols of propylene oxide plus 1 mol of glycerin is not inherently anywhere near at least 600. While it may be possible under certain reaction conditions to obtain a molecular weight of 600, the probabilities are small indeed and, in view of the fact that the method of preparing the condensation product is not set forth by Party Heiss and there is no basis on which to form even an opinion, and in view of the fact that it is recognized by several companies that the molecular weight cannot be calculated and in fact logic shows it cannot be calculated, it is submitted that there is no proper basis for the assumption of Party Heiss that the molecular weight is anywhere near the minimum critical figure called for by the counts in the interference.

"Where One Copies a Claim From an Issued Patent, It Should Clearly Appear That His Application Disclosed The Invention Either Expressly or Inherently"

It was held in the case of Hansgird vs. Kemner,

40 USPQ; 102 F. 2d 212; 26 CCPA 937:

"Where one copies claim from inadvertently issued patent, it should clearly appear that his application disclosed the invention either expressly or inherently; he may disclose invention by drawings, by use of language, or by reciting and teaching such subject matter as will inherently do thing or possess quality claimed for it; inherency may not be established by probabilities or possibilities; mere fact that certain thing may result from given set of circumstances is not sufficient, but, if disclosure is sufficient to show that natural result following from operation as taught would result in performance of questioned function, disclosure is sufficient."

The above case reaffirmed similar holdings in Parker vs. Ballantine, 26 CCPA (Patents); 101 F 2d 220; 40 USPQ 360; In re Ball, 28 USPQ 277; and McKee vs. Noonan, 32 USPQ 44;

24 CCPA; and 86 F.2d 986.

In the case of In re Ball, it was held that no dimensions are disclosed and while the structure may suppress arcing, structures strictly in accordance with the disclosure might be produced which would not suppress arcing and therefore function of suppressing is not inherent and applicant cannot copy claim calling for suppressing (28 USPQ 279).

In Brand vs. Thomas, 37 USPQ 505, 25 CCPA (Patents) 1053, 96 F. 2d 301, it was held

"Burden is upon applicant to show that he has clearly disclosed elements of counts before he will be permitted to extract from opponent's issued patent the invention in interference; lack of clear disclosure is not supplied by speculation as to what one skilled in art might do or might not do if he followed teaching of inventor; disclosure should be clearer than to suggest that one skilled in art might construct device in particular way; devices of parties and inventions respectively claimed and respective features disclosed are so different that counts would be out of place in application; no one writing claims originally in application would think of adopting language of counts; last consideration cannot be sole test because one takes out broad claims in patent will not be allowed to narrow them to avoid interference; counts call for alignment, but applicant does not show or describe alignment and alignment is not essential; but in other patents similar devices are shown in alignment and Patent Office found alignment; decision reversed by Court of Customs and Patent Appeals."

In the recent case of Spencer vs. Myers, 124 USPQ 175, (pg. 177) the Court of Customs and Patent Appeals reaffirmed the law in the above-cited cases.

In the present instance, it has been shown that the molecular weight of at least 600, a critical feature of the claims of the invention, is not disclosed in the application of the Party Heiss. Therefore, it is submitted that the interference should be dissolved for the reason that Party Heiss has no right to make the counts.

AS TO GROUND "b"

A study of the application of Party Heiss shows that the plasticizer such as the chlorinated diphenyl is an essential ingredient of his product. On pages 20 and 21 of his application, Party Heiss states,

"The plasticized products of the instant invention cannot be produced by first forming the polymerized or cured organic compound containing a urethane or thio-urethane group and then incorporating the cured product with the plasticizer. In order to obtain products having said properties, the organic compound containing the urethane or thiourethane group must be intimately associated with the plasticizer and then polymerized or cured to a higher molecular state."

It is seen therefore that a solid polyurethane product as called for by the claims of Party Price, interpreted in the light of the specification, was never contemplated by Party Heiss. The plasticizer is an essential ingredient of Party Heiss' composition and process and therefore must be included within any claims patentable to the Party Heiss as it has long been settled that one cannot omit an essential ingredient of his invention from his claims.

Under the rule of *Den Beste vs. Martin*, 116 USPQ 584, a party may for the purpose of interference be able to make a count even though after the interference the count would not be patentable to him. However, that opportunity only resides when the party copying the count has an example or species clearly falling within the count.

In the present instance, there is no example nor disclosure in the application of Party Heiss which has a molecular weight of at least 600. Inasmuch as each of the counts in the interference specifies a molecular weight of 600 for the condensation product of an alcohol having at least three hydroxyl groups with propylene oxide and inasmuch as Party Heiss has no

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such disclosure and no example coming within the claims, he cannot maintain the claims even for the purpose of determining priority.

It is submitted that the interference should be dissolved because all of the counts in interference omit an essential ingredient of the invention of the Party Heiss and also none of the counts reads upon any example or disclosure of Party Heiss.

Respectfully submitted,  
McCoy, Greene & TeGrote  
Attorneys

By J. H. TeGrote

Cleveland, Ohio  
March 30, 1960

PROOF OF SERVICE

A copy of this Motion to Dissolve has this 30<sup>th</sup> day of March, 1960 been forwarded by first class mail to the attorneys Heiss, listed below:

Clolle W. Upchurch, Esq.  
Penn-Lincoln Parkway West  
Pittsburgh 5, Pa.

McCoy, Greene & TeGrote  
Attorneys

By J. H. TeGrote

Enclosure:  
Excerpt of Dr.  
St. Pierre's Thesis

DEFENDANT'S EXHIBIT J

Certified copy Decision on Motions, dated August 15, 1960,  
Interference No. 90,414

Pages 919a to 925a

919a

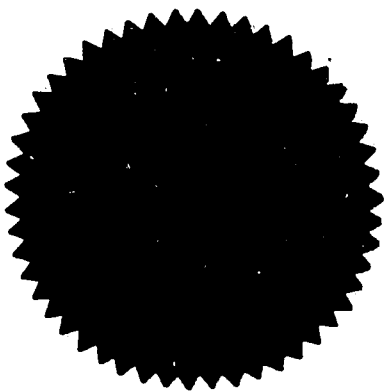
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PO-55-Rev  
(6-16-61)

U. S. DEPARTMENT OF COMMERCE  
UNITED STATES PATENT OFFICE

January 4, 1973  
(Date)

THIS IS TO CERTIFY that the annexed is a true copy from the records of this office  
of Certain Requested Documents, in Interference Number 90,414.



By authority of the  
COMMISSIONER OF PATENTS

*W. B. Walder*

*Certifying Officer.*



FORM 3

920a

Form No. 30

ADDRESSEE ONLY  
THE COMMISSIONER OF PATENTS  
WASHINGTON 25, D. C.

DEPARTMENT OF COMMERCE  
UNITED STATES PATENT OFFICE  
WASHINGTON

All communications respecting  
this case should identify it by  
number and names of parties.

Cza ja: kmw

Please find below a communication from the EXAMINER  
in this case.

*Robert C. Watson*

Commissioner of Patents.

Interference No. 90,414

Herbert L. Heiss

v.

Charles C. Price

MAILED

AUG 15 1938

Decision on Motions

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*Noted  
Mar 11  
2/11*

The party Price moves to dissolve this interference on  
the grounds (1) that the party Heiss has no right to make the  
claims forming the counts of the interference and (2) that the  
claims forming the counts of the interference are not patentable  
to the party Heiss.

Heiss opposes the motion to dissolve on the ground that  
his disclosure supports all of the limitations of the claims  
and is therefore entitled to make the counts for the purpose  
of contesting priority.

In the alternative Heiss presents a contingent motion to  
substitute counts H(1) to H(4) for present counts 3 to 6 in  
the event the Examiner affirms the party Price's motion to  
dissolve.

THE INVENTION

This invention relates to polyurethane polymers and a  
method of preparing same. These polymers are produced by  
reacting an organic diisocyanate with a condensation product  
of an alkylene oxide having from 2 to 4 carbon atoms and a

polyhydric alcohol having from 3 to 6 primary hydroxy groups, for example, the condensate of propylene oxide and pentaerythritol.

Counts 3 and 5, found below, are illustrative of the subject matter in issue:

Count 3

A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) a hydroxy terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide having from 2 to 4 carbon atoms and about .01 to 10 mol percent based on the alkylene oxide of a polyhydric alcohol having less than 7 carbon atoms and having 3 to 6 primary hydroxyl groups, at least 20 percent of said alkylene oxide having more than 2 carbon atoms, and (2) at least about an equal molar amount of an organic diisocyanate based on said polyether glycol, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether glycol polymer is formed.

Count 5

A product made according to process of count 3.

PRICE'S MOTION TO DISSOLVE

The party Price moves to dissolve this interference on the grounds (1) that Heiss has no right to make the claims forming the count of the interference and (2) the counts of the interference are not patentable to the party Heiss.

In support of ground (1) Price points out the following: That all of the counts of the interference require that the condensate has a molecular weight of at least 600 and that this

is a critical limitation, that Heiss fails to disclose condensates having a molecular weight of at least 600, and that the Heiss calculations showing a condensate of 13.2 moles of propylene oxide and 1 mole of glycerine as inherently having a molecular weight of at least 600, viz. 857, is an inaccurate assumption.

In support of ground (2) Price points out that a plasticizer such as chlorinated diphenyl is an essential ingredient of the Heiss product. It is urged that claims omitting this element are not patentable to Heiss.

HEISS' OPPOSITION TO THE  
PRICE MOTION TO DISSOLVE

In opposition to the Price motion to dissolve Heiss contends that the molecular weight limitation of the condensate "at least 600" is not in any way critical, that Heiss discloses a condensate having a molecular weight of at least 600, that the calculations of the propylene oxide-glycerine condensate are not in error and that Heiss is entitled to the counts for the purpose of contesting priority.

EXAMINER'S DECISION

The Price motion to dissolve is denied.

There is nothing in the file wrapper of the Price patent nor in the disclosure of the patent which establishes that the molecular weight of the condensate - "at least 600" is, in fact, critical and that molecular weights below this limit will not yield the desired results. Likewise, there is no

evidence on record which clearly supports the contention that the condensates of Heiss do not inherently possess a molecular weight of at least 600.

In the Price patent, column 2, lines 25 to 28 thereof, the statement ".....as low as 600" does not establish criticality of the molecular weight. This statement is considered to be presented for purposes of illustration only. At best, this limitation is part of a desired range only. There is no clear indication in the specification of the patent or in the file wrapper history that molecular weights falling without this limit are inoperative.

Since the mole ratios of alkylene oxide to polyhydric alcohol used by both Price and Heiss overlap it is reasonable to assume that Heiss inherently obtains a molecular weight of at least 600. It is immaterial that Heiss fails to show the method of preparing the condensate since these condensates are old and well-known, -- evidence the patents cited by Heiss and Price.

To support his contention that Heiss does not necessarily obtain condensates having molecular weights of at least 600, Price refers to various patents and a thesis by Dr. St. Pierre on the polymerization of alkylene oxides to show that reaction conditions, etc. govern the molecular weight of the final condensate. It is not seen wherein these references are determinative of this issue since, as pointed out above, the

molecular weight is not only not critical but also Heiss is not limited to any specific method of preparing his condensate.

Price, to further substantiate his position that Heiss does not obtain the required molecular weight, shows that when glycerine, containing 10% water, is reacted with propylene oxide a molecular weight below 600 is obtained. This assumption by Price as to the presence of 10% water is considered unjustified. It can reasonably be assumed that Heiss was working with relatively pure reactants. Any skilled polymer chemist realizes the necessity of employing substantially pure materials in polymerization reactions. Actually, Heiss states that his condensate is the reaction product of 13.2 moles of propylene oxide and one mole of glycerine; however, no water is mentioned.

Price further contends that the counts of this interference are not patentable to Heiss. A reading of the Heiss specification clearly indicates that the plasticizer need not be present when the polyurethane adduct is actually formed. The use of a plasticizer is considered not critical. For example, at page 7, lines 1 to 7 Heiss states that the polyurethane adducts may be preformed and then added to the non-reactive organic liquid (plasticizer). At page 18, lines 17 to 22 it is stated that the polyurethane is desirably prepared in the presence of a non-reactive organic plasticizer. A desired use is considered not to be critical. Obviously the plasticizer

is not essential to the reaction of the condensation product and the isocyanate. Furthermore, as pointed out by Heiss, the counts of the interference and the claims of the Price patent are open claims -- they do not exclude the use of a plasticizer. It should be noted, also, that when Price reacts the diisocyanate with the condensate, said reaction is carried out in the presence of a high boiling non-reactive organic solvent, which is not removed at the termination of the reaction.

THE HEISS CONTINGENT MOTION  
TO SUBSTITUTE COUNTS

In view of the fact that the Price motion to dissolve is denied, decision on the Heiss contingent motion is moot.

SUMMARY

The Price motion to dissolve on both grounds is denied.

No appeal (Rule 244-d).



Examiner, Division 50

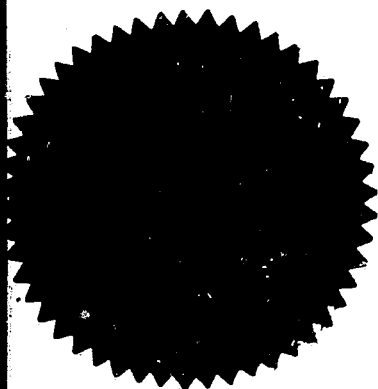
DEFENDANT'S EXHIBIT K

Certified copy of Petition for Reconsideration and  
Modification of Decision, dated August 22, 1960,  
Interference No. 90,414

Pages 926a to 930a

U. S. DEPARTMENT OF COMMERCE  
UNITED STATES PATENT OFFICEJanuary 4, 1973  
(Date)

THIS IS TO CERTIFY that the annexed is a true copy from the records of this office of Certain Requested Documents, filed August 22, 1960, in Interference Number 90,414.

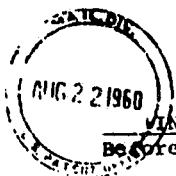


By authority of the  
COMMISSIONER OF PATENTS

*W. B. Walden*

*Certifying Officer.*





IN THE UNITED STATES PATENT OFFICE  
Before the Examiner of Patent Interferences

32  
Doc

CHARLES C. PRICE )

v. )

Interference No. 90,414

HERBERT L. HEISS )

PETITION FOR RECONSIDERATION AND  
MODIFICATION OF THE DECISION

The Party Price hereby petitions for reconsideration and modification of the decision of the Primary Examiner of Division 50, mailed August 15, 1960, in the above-identified interference.

Party Price specifically requests the Examiner to clarify his opinion and modify it by pointing out the portion of the Heiss application which he considers discloses a condensation product of a polyhydric alcohol having three or more primary hydroxyl groups with an alkylene oxide (at least in part) having more than two carbon atoms as specified in Counts 2, 3 and 5 of this interference.

Party Price has been unable to find the basis for any such glycol polymer in the Heiss application and Party Heiss has been unable even at the specific request of Party Price to point out the basis for such disclosure, yet the Examiner has held that it is disclosed. It is submitted that the Examiner should point out the portion, page and lines of the Heiss application upon which he based his decision. If the Examiner cannot find any basis, and it is submitted he cannot, then it is requested that his opinion be modified by dissolving the interference, certainly as to these counts.

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Intf. No. 90,414

Certainly a condensation product of 13.2 mols of propylene oxide and 1 mol of glycerine is no basis for Counts 2, 3 and 5, regardless of molecular weight consideration for glycerine has only two primary hydroxyl groups. Certainly the generic disclosure of a condensation product or condensate of pentaerythritol with an alkylene oxide is no basis for the above, for what is the alkylene oxide and what is the mol percent of pentaerythritol? Certainly the disclosure of triethanolamine plus alkylene oxide is no basis, for what is the ratio or what is the alkylene oxide?

It is submitted that Party Price is entitled to know upon what the Examiner bases his opinion. Party Heiss has been unable to inform Party Price of the basis for these counts. Regardless of the molecular weight, it is submitted that the interference as to Counts 2, 3 and 5 must be dissolved unless the Examiner or Party Heiss can point out where in the Heiss application there is basis for the glycol condensation product as defined in Counts 2, 3 and 5, even omitting the critical 600 minimum molecular weight.

The Examiner in his Decision listed Counts 3 and 5 as illustrative of the subject matter in issue. For easy reference, these counts are listed below:

Count 3. A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) a hydroxy terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide having from 2 to 4 carbon atoms and about .01 to 10 mol percent based on the alkylene oxide of a polyhydric alcohol having less than 7 carbon atoms and having 3 to 6 primary hydroxyl groups, at least 20 percent of said alkylene oxide having more than 2 carbon atoms, and (2) at least about an equal molar amount of an organic diisocyanate based on said polyether glycol, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether glycol polymer is formed.

Count 5. A product made according to process of Count 3.

Int'l. NO. 90,414

Count 2 is similar to Count 3 except that the polyhydric alcohol is specified as pentaerythritol.

It is seen from the above that each of these counts specifies that the polyether glycol having a molecular weight of 600 is a condensation product of .01 to 10 mol percent based on the alkylene oxide of a polyhydric alcohol having three to six primary hydroxyl groups. In Count 2, pentaerythritol has four primary hydroxyls.

The entire basis for any of the counts in Party Heiss' application is believed to have been considered the condensation product of 13.2 mols of propylene oxide with glycerin. Since glycerin has only two primary hydroxyl groups, it cannot be any basis for the above three counts.

It is unconscionable to permit the interference to proceed through the testimony period without the Examiner pointing out to Party Price upon what portion of the Party Heiss' disclosure he bases his holding that there is disclosed a condensation product of an alkylene oxide of more than two carbon atoms with .01 to 10 mol percent of any polyhydric alcohol having three or more primary hydroxyl groups. Party Price argued this in his briefs and at the final hearing.

The Examiner's holding that "as low as 600 molecular weight" in the Price patent is merely descriptive is believed to be clear error. When the patent points out that higher molecular weights are preferable but that those as low as 600 may be used, it is submitted that "600" is a limit, not mere preference, and

Intf. No. 90,414

that the 600 limit must be critical.

Respectfully submitted,

McCoy, Greene & TeGrotenhuis  
Attorneys

By 

Cleveland, Ohio

August 19, 1960

SERVICE

A copy of this Petition for Reconsideration and Modification of the Decision has this 19th day of August, 1960, been forwarded by first class mail to the attorney of Party Heiss, listed below:

Clelle W. Upchurch, Esq.  
Penn-Lincoln Parkway West  
Pittsburgh 5, Pa.



DEFENDANT'S EXHIBIT L

Certified copy of Decision on Petition for Reconsideration,  
dated October 3, 1960

Pages 931a to 933a

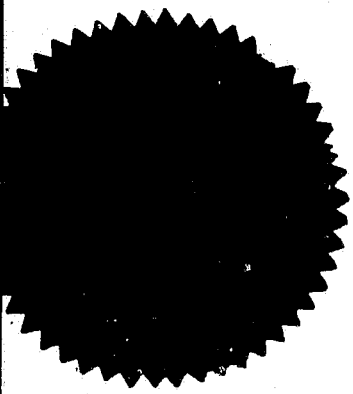
PO-55-Rev  
(6-16-61)U. S. DEPARTMENT OF COMMERCE  
UNITED STATES PATENT OFFICEJanuary 4, 1973  
(Date)

THIS IS TO CERTIFY that the annexed is a true copy from the records of this office  
of Certain Requested Documents, in Interference Number 90,414.

By authority of the  
COMMISSIONER OF PATENTS

*W. B. Tisdale*

*Certifying Officer.*



932a

PAPER No. 37

ALL communications respecting  
this case should identify it by  
number and name of petitioner.

DEPARTMENT OF COMMERCE  
UNITED STATES PATENT OFFICE  
WASHINGTON

Czaja:kmw

Please find below a communication from the EXAMINER  
in this case.

*Robert C. Watson*

Commissioner of Patents.

MAILED

OCT 3 1960

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Interference No. 90,414

Herbert L. Heiss

v

Charles C. Price

Decision On Petition  
For Reconsideration

The Petition for Reconsideration of August 22, 1960 by the party Price is treated as a request for reconsideration of the Decision on Motions of August 15, 1960, (Paper No. 30) in accordance with Section 1105.07 M.P.E.P. In said decision Price's motion to dissolve was denied.

As a basis for reconsideration Price contends that Heiss' application has no basis for a condensation product of a polyhydric alcohol having three or more primary hydroxyl groups with an alkylene oxide having more than two carbon atoms, (at least in part), as specified in counts 2, 3 and 5 of this interference.

The petition of the party Price to modify the Decision on Motions by dissolving the interference is denied.

The Heiss' specification clearly provides basis for counts 2, 3 and 5. At page 3, lines 4 and 5 and lines 10 and 11, Heiss discloses "alkylene oxide condensates of glycerine, triethanol amine" and "alkylene oxide condensates of pentaerythritol",

Interference No. 90,414 -2-

respectively. In various working examples, including examples 10, 11 and 12 among others, propylene oxide-glycerine condensates are disclosed. It is manifest, therefore, ~~that~~ in view of the disclosure on page 3 and the working examples, that pentaerythritol and triethanol amine may be used in lieu of glycerine in preparing the condensates with propylene oxide; triethanol amine and pentaerythritol are polyhydric alcohols having 3 or more primary hydroxyl groups.

The Examiner is still of the same opinion as to the "600 molecular weight" limitation as set forth on page 4, lines 4 to 11 of his Decision On Motions.

Reconsideration of the Examiner's Decision has been given but no change is made thereto.

The Examiner has taken cognizance of U. S. Patent No. 2,948,691, issued to Windemuth et al (filed on May 6, 1952) which shows condensates of ethylene oxide and trimethylolpropane or pentaerythritol reacted with an organic polyisocyanate.

No appeal (Rule 244-d).

  
Examiner, Division 50





DEFENDANT'S EXHIBIT M

Certified copy of Brief in Interference No. 90,414

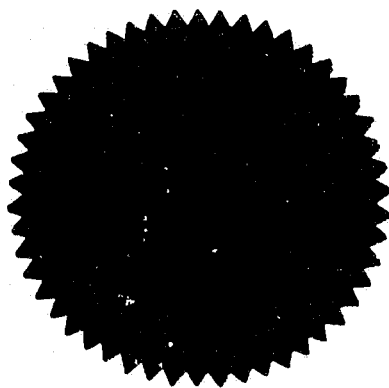
Excerpts - Cover sheet and first two pages

Pages 934a to 936a

U. S. DEPARTMENT OF COMMERCE  
UNITED STATES PATENT OFFICE

January 4, 1973  
(Date)

THIS IS TO CERTIFY that the annexed is a true copy from the records of this office of Certain Requested Documents, filed August 23, 1961, in Interference Number 90,414.



By authority of the  
COMMISSIONER OF PATENTS

*W. B. Walden*

*Certifying Officer.*



IN THE UNITED STATES PATENT OFFICE  
Before the Board of Patent Interferences

90414 - 58

AUG 24 1961

CHARLES C. PRICE )

Vs. )

HERBERT L. HEISS )

Interference No. 90414

BRIEF FOR PRICE

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DEFENDANT'S EXHIBIT 7

Heiss Notebook - June 27, 1951 - October 31, 1951

Excerpts-Pages 73323 - 73326  
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MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73323

PROJECT Polysynthetic resinDATE Sept 4 1951PROJECT NO. 171-741SIGNATURE Robert L. Weiss

HIGGINBOTHAM &amp; SAWYER

## ABL Project.

Attempt to prepare materials from 1 mol glycol or polyglycol and 2 mols diisocyanate to yield large molecules with active NCO groups at each end. This may be of value as propellant adhesive.

Sept 4 Mix reactants at room temp. Cool in ice water. Allow to stand overnight.

	Reactant	Mol wt	Av. wt	Equip.
A	1,2-Ethylene glycol TDE	194 174	19.4 34.8 + 3	.2 .4 +
B	Trimethylene glycol TDE	150 174	15.0 34.8 + 3	.2 .4 +
C	Diethylene glycol TDE	106 174	10.6 34.8 + 3	.2 .4 +
D	Ethylene glycol TDE	62 174	6.2 34.8 + 3	.2 .4 +
E	Tripropylene glycol TDE	112 174	11.2 34.8 + 3	.2 .4 +
F	Diisopropylene glycol TDE	134 174	13.4 34.8 + 3	.2 .4 +
G	Propylene glycol TDE	76 174	7.6 34.8 + 3	.2 .4 +

The ethylene series was miscible with the TDE but cleared as the reaction commenced (5-10 min). It cleared that the lower the mol wt of the polyglycol, the longer it took to clear up.

The propylene series were all compatible except the mono propylene glycol. This reacted slowly to form a white solid material.

A 3% excess of isocyanate was used in each case to insure complete reaction of glycol and to account for any traces of moisture.

NEXT PAGE 937

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73324

PROJECT Isocyanate prepDATE Sept 5-11 1951PROJECT NO. 171-741SIGNATURE Arthur H. Case

HIGGINBOTHAM &amp; SAWYER

Sept 5 - Contd from 73323

All materials except 73323 D were either viscous liquids or masses at room temp. D was an opaque white solid. Each sample was heated to 100-120°C with infra red lamp and subjected to 3-6 mm vacuum until all gas and vapor evolution ceased. This should remove most of the excess TDI.

Sept 6 - Vacuum distillation as above.

Sept 7 Vacuum dist as above.

Sept 10. Vacuum dist as above.

Materials now appeared as follows:  
A, C, E, F were clear, amber glasses  
B - a very viscous, clear, amber material  
G - an opaque, white mass of heavy consistency.  
D - a translucent amber glass

Sept 11 B D G sent out for determination of amine equivalent to see whether or not free-NCO groups are actually present.

CONCLUSIONS

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73325

PROJECT Isocyanate Appl  
PROJECT NO. 171-741  
MISSISSAUGA & LAWYERDATE Sept 10 1951SIGNATURE W. H. Jones

- ABL Project  
See 73323..  
Sept 10 This experiment to compare high yield of  
isocyanate & reacting 1 mol anhydrous glycerine  
with 3 mols TDZ

Material	Am't	Exptl	Yield
TDZ	26.1g + 3	10+	15+
glycerine (anhyd)	46	15	05

Reactants mixed at room temp for 30 min. No  
reaction as evidenced by continued unreactability  
and no heat evolution. Added about 1 ml pyridine  
immediately. Exothermic reaction was initiated.  
Covered container in ice water and allowed to  
stand, shaking occasionally. Solution (dispersion)  
became more and more viscous and became cloudy.

Sept 11 Upon standing overnight, the material was  
a cream-colored solid mass. This was  
subjected to 3-6 mm vacuum at 100-120°C (infra red  
lamp) until all bubbling ceased, indicating  
removal of pyridine and excess isocyanate.

Sept 12 Upon completion of above distillation,  
the material was cooled and became a  
clear, amber glass. This sent out for amino  
equivalent determination (see 73324).

## CONCLUSIONS



MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73326

PROJECT Isocyanate BondDATE Oct 13 1957PROJECT NO. 171-741SIGNATURE John H. Jones

HIGGINBOTHAM &amp; SAWYER

ABL project

Test 13 - Preliminary work with microcellulose-cellulose acetate adhesives.

We now have on hand the following materials:

1. 1" x 1/8" discs of rocket propellant from ABL
2. cellulose acetate (Monsanto FEO) of various types used as propellant inhibitor (received from ABL)
3. ethyl cellulose of the type being considered as an inhibitor (received from ABL)
4. polyethylene (Monsanto Lustrax LT) received from Springfield. This is another possible inhibitor.

On order are additional specimens of cellulose acetate (CA), ethyl cellulose (EC) and microcellulose (MC) to permit testing, supplement using all our stocks of specific materials from ABL.

Bonding Agent	CA to CA	Materials Bonded. (cured 6 min in press 2 hrs)	CA to propellant
A- acetone	good	poor	sep at interface
B- 10% CA in acetone	good	poor	"
C- B + 1% TDI	good	fair	separated interface and within propellant
D- C + 1% pyridine	poor	very poor	sep at interface
E B + 1% 73323 F	fair	-	-
F F + 1% pyridine	good	-	-

The above samples were placed together and clamped together under gentle pressure in a vise for the 2 hour cure at room temp.

## CONCLUSIONS

Presence of pyridine in TDI contains adhesive results in formation of yellow amorphous material, resulting in bad adhesion. Evidently polymerization of TDI occurs prior to desired reaction with cellulose acetate surface.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73328

PROJECT Isocyanate App.DATE Oct 19 1957PROJECT NO. 171.741SIGNATURE John L. Hess

HIGGINBOTHAM &amp; FAWCER

ABL Project 73326

Sept 19. Experimented with the propellant discs received from ABL (73326-1). The surface of these discs is slightly pitted - not entirely smooth, due to the method of preparation. After 5 minutes of meeting Paul Fagne at Cincinnati, Aug 31, by H. L. Weiss upon getting a portion from the disc and exposing a fresh surface one can see particles of nitrocellulose dispersed in the soft nitrocellulose-nitroglycerine phase. This type of composition was found to limit the use of solvents in any proposed adhesive. Tests wherein small amounts of methanol, acetone, or fulvene were placed on the propellant indicated that the nitroglycerine containing portion was much more soluble in these solvents than the nitrocellulose. This resulted in a concentration of nitroglycerine upon the surface after the solvent evaporated. This phenomenon will naturally make adhesion problems more complicated.

It is possible, but not probable that an adhesive can be prepared without solvent. In this case we would be limited to a solvent which would serve as an excellent vehicle for the adhesive, but would not excessively attack the propellant. Some of the higher aliphatic solvents may serve this purpose. The disadvantage here would be that such a solvent would probably have little effect on the cellulose acetate surface, and this would tend to decrease adhesion at this interface.

Aids for the problem of obtaining an adhesive, there is the question of procedure of covering the propellant. It has occurred to me that another way of doing the whole thing would be to laminate a sheet of nitrocellulose to a sheet of cellulose acetate or ethyl cellulose. This could then be placed inside the mould and the resin formed therein. Since the nitrocellulose surface of the laminated sheet would be next to the nitrocellulose granules, and the whole gelled with nitroglycerine, there should be no adhesion problem here.

## CONCLUSIONS

Using isocyanates (possibly methanes) as the laminating adhesive would also present a barrier to nitroglycerine migration.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73336

PROJECT Isocyanate OxydDATE Oct 1 1955PROJECT NO. 171-741SIGNATURE Robert J. Jones

HIGGINBOTHAM &amp; SAWYER

ABL Project

Oct 1 Solubilities of TDI-polyol condensation products  
about .5 gram of product placed in 3 ml solvent  
and allowed to stand (occasional shaking)  
for 16 hrs. Observed for solubility. Tubes then returned  
to holding set of solvent and allowed to stand  
4 hrs. Again observed.

Compound.	n-Hexane		Benzene		Acetone	
	Cold	Hot	Cold	Hot	Cold	Hot
73323 A	insol		part. sol.		sol	
" B	"		"		"	
" C	"		"		"	
" D	"		insol		insol	
" E	"		part. sol.		sol.	
" F	"		sol.		sol	
" G	"		insol		insol	
73325	"		insol		insol	
73332	"		sol.		sol	
73333						
73335	insol		sol		sol	

It may be of interest to note that typical condition  
of products show that they have had a chance to  
reach equilibrium:

73323 A	soft viscous fluid	73325	hard brittle glass
B	stiff viscous fluid	73332	soft viscous fluid
C	" " "	73333	" " "
D	hard brittle glass	73335	hard brittle glass
E	" " "		
F	" " "		
G	stiff, white paste		

## CONCLUSIONS

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73337

PROJECT Monomale Cond  
PROJECT NO. 171-741  
HIGGINBOTHAM & SAWYER

DATE 10-8-57 1957SIGNATURE Robert H. Kress

ABL project - evaluation of adhesives

Oct 2 - Prepare 10% soln of TDI-polyol condensate in anhydrous benzene. This solvent chosen because it has little effect on cellulose acetate, and any adhesive bond will be due to the condensate, not solvent action of benzene on the CA surface.

Solution designation.

A  
B  
C  
E  
F  
2  
5

material dissolved (10% soln).

73323 A

" B

" C

" E

" F

73332

73335

Observations of this strength, do not suggest a heavy enough film of active agent + too soft material. This situation is aggravated by the relatively non-uniform surface of the propellant.

Attempted to form TDI-polyol products in situ and to compare these to prepared materials. Used ethylene glycol 1,3 as it is compatible with TDI and poses no mixing problem.

A thin film of TDI liquid was applied to the propellant surface, and a thin film of ethylene glycol 1,3 to the cellulose acetate. The two surfaces were then brought into contact and clamped under slight pressure. Cure was 1 hr @ 50°C. After being allowed to come to room temp. the CA was peeled from the propellant. The bond was brittle and broke fairly easily, separating at the propellant-adhesive interface.

When 73332 was applied to each surface and the assembly cured as above, a better bond was created. This resulted within the adhesive, indicating improved adhesion to each surface.

CONCLUSIONS

Adding bases of residue to 73332 immediately before joining the surface greatly catalyzed its reaction with ethylene glycol 1,3, and excessive foaming resulted. Bond was still poor, however.

See next page

943

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73338

PROJECT Isocyanate Cure  
PROJECT NO. 171-241  
HIGGINBOTHAM & SAWYER

DATE Oct 1957  
SIGNATURE [Signature]

Cut from p 73337

Other bonds were made using impurities at even the terminal -OH groups (as in 73334 and C) it was thought that this might give a more flexible film of adhesive which would respond better to applied stresses. Results were the same as in the case of 73332, however.

These tests reveal two main difficulties:

1- The adhesive layer reacts with atmospheric moisture (or at least absorbs enough moisture) during the brief interval preceding joining of the surfaces so that during the cure, excessive gas evolution occurs. This creates many small bubbles in the adhesive layer, weakening the bond.

2- The cured adhesive is excessively brittle. This prevents the distribution of strains within the layer when stress is applied, making the bond susceptible to failure at the point of stress with consequent rupture of the entire bond. A more elastic layer will reduce this effect.

The second deficiency is more basic than the first. The first may be remedied by procedure and will be in the next batch. The second defect is of a qualitative nature. MDI will be evaluated as a substitute for TDI in the hope that the increased separation of the -NCO groups will promote flexibility of the urethane.

CONCLUSIONS

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73339

PROJECT Monomer's CopolDATE Oct 4 - 5 1951PROJECT NO. 171-741

HIGGINBOTHAM &amp; SAWYER

SIGNATURE Robert F. Davis

ABL project - see p 73323

Oct 4 - MDI-diol adducts to form high mol wt desoxyantracene.

	Reactant	AmL	Mol:	
A	terephthylene glycol MDI (Dm)	9.7 g 25.0	.05 0.10	vigorous exothermic reaction yields soft amber resin.
B	triethylene glycol MDI (Dm)	7.5 25.0	.05 0.10	as above -
C	diethylene glycol MDI (Dm)	5.3 25.0	.05 0.10	exothermic reaction, yields pale, amorphous solid
D	ethylene glycol MDI (Dm)	3.1 25.0	.05 0.10	sluggish reaction, requires heating, yields yellow amorphous product.
E	styrene glycol (Dm) MDI	6.9 25.0	.05 0.10	Heat to melt glycol. Reaction proceeds to yield hard amber resin.

Reaction as follows. Melt MDI in small container  
and add diol. Mix well - keeping MDI molten. Reactions  
usually completed in 30 minutes - allow to cool to room  
temp.

Oct 5. These materials are more elastic than those  
made with TDI, and should show more resistance  
as adhesives.

## CONCLUSIONS

MDI- $\alpha$ -glycol adducts show more possibilities as  
adhesive components than those made with TDI.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73341

PROJECT Isocyanate ApplicationDATE Oct 5-10 1957PROJECT NO. 171-741SIGNATURE John H. Davis

BSINBOTHAM &amp; SAWYER

ABC project - see 73339  
A Oct 5.

Since higher mol wt polyglycols seem to react with MDI to form stickier materials, further reactions to be made with some yet higher mol wt materials.

Material	Amt	Mols
MDI	25.0	.10
polyethylene glycol 600 (Carbide & Carbon)	39.0	.05

Heat MDI, add polyethylene glycol and mix well. Cool, pouring exothermic reaction. Excess heat evolution takes place.

B Oct 9. Modified reaction as in 73342 B. Upon preliminary heating to 175°C, the 30.0g of glycol lost about 0.6g weight. Not many bubbles appeared upon addition of 2g MDI. After 30 minutes, remainder of MDI was added to hot glycol to insure melting and good mixing of the MDI. Slow evolution of bubbles. The product is an opaque brown, rubbery material containing specks of (apparently) MDI polymer.

Oct 10-

This adduct, when spread in a thin film, does not bubble up nearly to the extent of 73342 B. It dries to a rubbery film which adheres well to glass and metal.

The use of polyglycols of higher molecular weight appears to approach the solution to this problem. It would seem that formation of high molecular weight isocyanate would offer additional advantages. In view of the fact that long chains are desirable, ethylene oxide condensates, with tri- and (and other poly)ols, such as, triethylamine, glycerine, pentaerythritol, etc, should form interesting addends for di or polyisocyanates.

CONCLUSIONS

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73342

PROJECT Carbamate AnalDATE Oct 5 - 10 1957PROJECT NO. 171-741SIGNATURE Robert H. Weiss

HISBINGHAM &amp; SAWYER

A Alt project  
O.T.S. TDI adducts for comparison to MDI adducts  
on 73341

Material	wt	nds
TDI	17.4 g	0.10
polyhydroxyethyl Glycol (Carbide Carbon)	30.0 g	.05

Mix at room temperature and cool during any exothermic reaction. Excess gas evolution.

Oct 8. The above gas evolution seems to be connected with the bubbling of adhesives (see 73338-1) during curing. This may be due to moisture content, or acid value of the polyglycol, however these values are low (as given by the manufacturer). Drying of the glycol will be investigated, however.

- B- Using same amounts of reactants as in A above, after procedure. Weigh out polyglycol and heat to 175°C. Only small amounts of bubbles are observed. Add 1g TDI to react with moisture, and maintain temp. at 165-175°C. Considerable gas evolution, when bubbling diminishes (after 30-40 minutes), cool to room temperature, add remainder of TDI, mix well and cool in water bath, keeping temp. below 50°C. After reaction has commenced (evidenced by increasing viscosity) heat slowly to 150°C to complete reaction. Some gas evolved, but much less than in A. allow to cool to room temp.
- This method has the advantage of removing the moisture with a small amount of TDI without thickening of the mixture. Thus more complete reaction is possible. After most of the water is thus removed, the addition reaction can proceed and the mass will not foam up in the container.
- The material is a viscous, clear, amber liquid

## CONCLUSIONS

Oct 10 This product has more tendency to foam when exposed to the atmosphere than does 73341B. Both products produce rubbery films.



MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73343

PROJECT Monomethyl  
PROJECT NO. 73-711  
SMITH & SAWYER

DATE Oct 11-15 1957SIGNATURE [Signature]

ABL project - all 73341 and 73342

Oct 11. Material Amt Mols  
MDI 25.0g 0.10  
Carbowax 1000 W 50.0 .05  
(Carbide: Carbon)

Same procedure as 73342 B. Preheat bubbling during pre-heating of liquid apparatus. Considerable bubbling during preliminary MDI reaction.  
Final product an opaque, brown, rubbery material very similar to 73341 B.

Material Amt Mols  
MDI 25.0g 0.10  
Carbowax 1500 W 75.0 .05

Same procedure as 73342 B. Little bubbling during preheat and preliminary MDI reaction. Considerable gas evolution during main reaction.  
Final product is a clearly, orange, viscous liquid.

Material Amt Mols  
TDI 17.4g 0.10  
Carbowax 1000 W 50.0 .05

73342 B reaction (see A above).  
Final product a viscous, clear, yellow liquid.

Material Amt Mols  
TDI 17.4g 0.10  
Carbowax 1500 W 75.0 .05

See B above

Product a clear yellow liquid less viscous than C (above).

Upon standing it can keep 73.3 D becomes cloudy, containing small particles of solid, white material.

CONCLUSIONS

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73344

SUBJECT Oxycarbonyl Compd  
SUBJECT NO. 121-241

DATE Oct 12, 1957SIGNATURE Hebert

ABT project - preparation of high mols. wt. tri-  
isocyanates by direct reaction of TDI or MDI with  
glycerine-EO\* condensation \*

Oct 12 A-  

Material	Wt	Mols
TDI	26.18	.15
glycerine-EO*	26.6	.05

Procedure - see 73342B - Inexpedient reaction  
forming hard, infusible product. Needs more  
moderate procedure.

B  

Material	Wt	Mols
MDI	37.5	.15
glycerine-EO*	26.6	.05

Procedure: see 73341B - as above.

Oct 15 It is probable that the above reaction can  
be run more readily in solvent media. Since  
the product (adduct) will however be a hard  
material, insoluble of being washed to a  
surface without use of solvents, it will not  
be prepared at this time.

## CONCLUSIONS

\* Glycerine-EO condensation  
1 mol glycerine + 10 mols EO prepared by  
Hebert & Co. on 20, 1950 NB reference

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

N<sup>o</sup> 73345

PROJECT Isocyanate Compd  
PROJECT NO. 131-741  
MONTAN & SAWYER

DATE Oct 15 - 16 1951SIGNATURE Harold F. Weiss

ABL Project

Evaluation of isocyanate - polyol - adducts.

<u>NB no.</u>	<u>addenda</u>	<u>comp / adduct</u>	<u>prop / foam.</u>
73342 B	TDI- polyethylene glycol 600	viscous amber liquid	light colored, rubbery, fine, many bubbles.
73341 B	MDI- polyethylene glycol 600	thick, brown liquid	brown foam softer than 73342 B. Tendency for some large bubbles, more volume than 73342 B
73343 C	TDI- Carbowax 1000 W	viscous, amber liquid	light colored foam very uniform bubblelike slightly softer than 73342 B
73343 A	MDI Carbowax 1000 W	rubbery, brown solid	amber foam with nice uniform bubbles more volume than 73343 C
73343 D	TDI Carbowax 1500 W	waxy, yellow solid water soluble	does not foam
73343 B	MDI Carbowax 1500 W	waxy, brown solid water soluble	does not foam

The above forms are readily formed at room temperature in 8-16 hrs. By adding traces of pyridine and warming to about 50°C, reaction will be completed in about 30-60 minutes.

**CONCLUSIONS**

Properties of foams can be tailored to various specifications by use of various polyols of isocyanates. TDI with polyethylene glycols of about 600 mol wt seem useful. It is suggested that MDI will be best when used with lower mol wt polyols.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73346

OBJECT Isocyanate TestDATE Oct 17-18 1957OBJECT NO. 171-741SIGNATURE [Signature]

SMITH &amp; SAWYER

ABX project

Oct 17-

Material	wt	in.
TDI	34.8 g	0.2
polyethylene glycol	30.0	.05
tetraethylene glycol	9.7	.05

Blend - 100% heat to 175°C to drive off any possible moisture. Cool down? add TDI mix with stirring. Some gas evolution. After initial reaction, cool down, heat to 175°C to drive to completion. Product is a clean, amber, viscous liquid.

This product approaches a 50-50 blend of 73342B and 73323A. As expected the resulting foam is not as good as between these two. The foam, is light colored, firm, yet flexible, and has a greater volume, and foams more readily than 73342B.

- The following questions remain to be answered:
1. Is a blend of glycols superior to the use of one? Equal of water hydrate and urea?
  2. General use of MDI and a polyglycol of lower average mol wt produce superior foams to TDI and a polyglycol of higher average mol wt? Such an MDI product should be more hydrophobic and less EO. Links would be contained in the molecule.
  3. Will the presence of excess TDI (or MDI) improve foaming action and result in superior foams?

Oct 18- A 1/4" square section of ABX prepellant was cemented between two 1" x 1 1/2" sections of Fabrics FEO cellulose acetate. 73346 plus a trace of prepellant was used, and cured 1 hour at 50°C. After cooling to room temp, the bond ruptured at 20 lbs load. This amount to 300 lbs/sq in. Larger test pieces with less edge effect also showed still higher strengths.

## CONCLUSIONS

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73347

JECT *See serials 1-4*JECT NO. *171-741*

GOTHAM &amp; SAWYER

DATE *9-11* 19 *57*SIGNATURE *Robert F. ...*

ABZ Project: see 73346 and 73343

A Material  
TDI 34.8g 0.2  
polyethylene glycol 400 20.0 0.1

Same reaction as 73341 - B. Product is a clear amber glass.

B TDI 34.8g 0.2  
polyethylene glycol 200 20.0 0.1

React as above. Product is a clear amber glass. Excellent cohesion glass. Good shock resistance - difficult to pulverize with hammer.

C TDI 34.8g 0.2  
polyethylene glycol 19.4 0.1

React as above. Darker-colored than 73347 B

D MDI 50.0g 0.2  
polyethylene glycol 400 20.0 0.1

React as in 73341 B. Product is a thick viscous, stringy material.

E MDI 50.0g 0.2  
polyethylene glycol 200 20.0 0.1

React as in D. Product is a cloudy, brown glass.

F MDI 50.0g 0.2  
polyethylene glycol 19.4 0.1

React as in D. Product is a cloudy brown glass.

CONCLUSIONS

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73348

PROJECT Cellulosic AdhDATE Oct 23-24 1951PROJECT NO. 171-741SIGNATURE [Signature]

ABT Project - see 73347

Oct 23. - Comparison of material made of C-cured glycols with one made with glycol of intermediate mol wt.

A	Materials	Cent	Wt's
	TDI	34.8 g	0.2
	polyethylene glycol 200	10.0	0.05
	600	30.0	0.05

React by procedure 73342 B

B	Materials	Cent	Wt's
	TDI	50.0	0.2
	polyethylene glycol 200	10.0	0.05
	600	30.0	0.05

React by procedure 73341 B.

Oct 24. Attempts to reduce foaming of adhesive:

A 50% by wt solution of 73346 in Cylene was prepared (C). Also prepared was a similar solution containing 2.5% p-methoxyphenol. These solutions were used to cement 2 pieces of cellulose acetate together in the following manner:

Method of Cementing	using C	using D
1. apply solution to each surface, let solvent evaporate, press together, cure 2 hr @ 50°C	few bubbles - incomplete cure - fair adhesion	few bubbles - complete cure - good adhesion
2. place film of ethylene glycol over adhesive before pressing together. Cure as above	few bubbles - incomplete cure - poor adhesion	few bubbles, incomplete cure, poor adhesion
3. spread adhesive layer to steam before pressing together. Cure as above.	foamed - complete cure, good adhesion	foamed, complete cure, excellent adhesion
<del>4. place film of ethylene glycol over adhesive layer before pressing together. Cure as above.</del>	<del>few bubbles - complete cure at room temp, good adhesion</del>	<del>few bubbles, complete cure at room temp, good adhesion</del>

foamed bonds more elastic and shock resistant than the unfomed ones. 953

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 73349

PROJECT Monomer TypeDATE Oct 25 - 27 1951PROJECT NO. 171-741SIGNATURE Robert J. Sawyer

SABOTHAN &amp; SAWYER

Oct 25 ABZ prepared  
Prepared 50% adducts with increasing adducts  
in anhyd. benzene. Solutions designated (P) also  
contain 5% pyridine

			adduct composition
A, AP	73348 A	solution in benzene	TDI 200-600
B, BP	73347 A	" " "	" 400
C, CP	73342 B	" " "	" 600
D, DP	73348 B	" " "	MDI 200-600
E, EP	73347 D	" " "	" 400
F, FP	73341 B	" " "	" 600

Oct 26 - Rec p73348

The above solutions were applied to cellulose acetate pieces 1" x 1/2" x 1/8". solvent was allowed to evaporate (about 5 minutes). The pieces were pressed together and cured for 1 hr @ 50°C, no pressing applied during cure. Pairs of pieces were also cemented with the above starting materials (C, not 50% adducts) and given a similar cure. Certain assemblies did not cure completely, in 1 hr. All pieces were allowed to stand at room temp over the weekend so that final, ultimate separation and strength could be compared.

Oct 27

Results of above tests.

	100% adduct	50% adduct in benzene	50% adduct in benzene plus 5% pyridine
7348A	not cured in 1 hr @ 50°C irregular air pockets adhesion ①	not cured in 1 hr @ 50°C irregular air pockets adhesion 3	irregular air pockets adhesion 3
7347A	not cured in 1 hr @ 50°C irregular air pockets adhesion ①	not cured in 1 hr @ 50°C irregular air pockets adhesion 3	large (2-3mm) bubbles adhesion 4
7342B	not cured in 1 hr @ 50°C large (2-3mm) bubbles adhesion 3	various sized bubbles adhesion 4	few small bubbles adhesion 4
7348B	fine (<1mm) bubbles adhesion ①	not cured in 1 hr @ 50°C large (4-5mm) bubbles adhesion 4	various sized bubbles adhesion 4
7347B	fine bubbles adhesion 3	large (2-3mm) bubbles adhesion 4	medium (1-2mm) bubbles adhesion 4
7341B	not cured in 1 hr @ 50°C fine bubbles adhesion 3	large (2-3mm) bubbles adhesion 4	medium (1-2mm) bubbles adhesion 4

Adhesion ratings: 1 is best, 4 is worst (no peel). A rating of ① is equivalent to about 60-70 lbs per sq. inch.

DEFENDANT'S EXHIBIT AA

Heiss Notebook - October 31, 1951 - February 18, 1952

Excerpts - Pages 75858  
75863  
75864  
75881  
75883  
75884

Pages 955a to 960a



MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LANSING, MICHIGAN

WP 75858

PROJECT Isocyanate AdductsDATE Nov 14 1957PROJECT NO. 171-741SIGNATURE Robert L. Davis

ROBERT L. DAVIS

Diisocyanate - polyol adducts.

Nov 14

Due to the similarity between these materials and the German diisocyanate - polyester adducts (as used in Vulcolons, for example), it might be wise to consider their uses in broader scope. This would appear to offer three advantages at least:

1. Easier circumvention of the German Vulcolon patents
2. The ether linkages of the polyglycol adducts should be more stable than the ester linkages of the polyesters. These latter seem to be less resistant than the urethane linkages in the Vulcolons, and an elimination of these weaker bonds should improve overall product stability.
3. The use of polyglycols (or other ethylene or propylene diol condensates) offers unlimited variety in building up molecules of various degrees of linearity or nonlinearity.

Nov 14. ABL project - Effect of excess diisocyanate content on foam formation.

It is probable that the isocyanate - polyglycol adducts prepared in this lab contain some excess isocyanate, as it was desired to avoid an excess of the glycol. It is quite possible that this excess of isocyanate is causing excessive foaming during adhesive cure. It will be advantageous to know the effect of this excess, both from the standpoint of reduced foaming of adhesives or debonders and resolution in the case of foams.

Varying amounts of TDI were added to representative TDI and MDE adducts and the resulting foams compared. 2 drops pyridine (ca 0.1 gram) were added to the mix, and curing performed for 1 hr at room temp. followed by 1 hr at 50°C.

See next page.

CONCLUSIONS

955

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 75868

PROJECT Acrylonitrile Copoly.DATE May 20-23 1957PROJECT NO. 171-741SIGNATURE Robert H. Hearn

RESEARCHMAN &amp; CHEMIST

HBL project - TDI-(glycerol-EO condensate) adduct. See 73344

A	9m, 20 -	Material	Amt	Wts
		TDI	26.1 g	.15
		glycerine-EO	26.6 g	.05
		anhyd acetone	200.0 g	solvent.

To a three neck 500 ml flask fitted with reflux condenser, stirrer, and dropping funnel, add the TDI and 150g acetone. Remove 50g acetone for running out dropping funnel. Heat to reflux and add glycerol-EO dispense from funnel at a rate of about 50g per hour. Vigorous agitation.

After about half the glycerol-EO has been added (15 minutes) the liquid suddenly becomes viscous and turns into a chunky soft solid. Addition of remaining glycerol-EO is terminated and the remaining acetone added. Solid does not all go back into solution although the acetone is converted into a heavy gel in which are dispersed pieces of the white solid. Added another 150g acetone and stirred. Allow to stand overnight without agitation.

Nov 24 The solid appears to have coagulated out from the acetone - the acetone is thin and no longer viscous. Decant off the acetone and add 200g chloroform. Reflux with stirring. The solid swells but does not go into solution. This approach abandoned.

B Repeat above experiment using 200g dioxane instead of acetone. Probably due to higher reflux temp, reaction commences immediately the glycerol-EO is added. After 30 minutes, all glycerol-EO is in and heating is continued for an additional 30 minutes. The mixture is a viscous, opaque, yellow material.

Nov 23. Distill off dioxane under reduced pressure (BP 40°C). The product was only limited solubility, and turned to thick, viscous dispersion of small particles in what was apparently a poor solvent vehicle.

## CONCLUSIONS

This type adduct is too insoluble to be of much use, however it may be possible to blend it with a polyglycol. It may be possible to react isocyanate with a mixture of alcohol and glycerol-EO.

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

REF 75864

PROJECT Isocyanate Appl.

DATE July 23, 1957

PROJECT NO. 121-741

SIGNATURE Robert H. Lewis

MONSANTO & BAYNE

ABT project - ACC 75863

To prepare isocyanate (MDI) adduct of mixed polyethylene glycol 400 and glycerol - EO.

A 7/23-	Materials	Wt	Moles
	MDI	50.0g	0.2
	polyethylene glycol 400	30.0	.075
	glycerol EO	13.3	.025

1. see 75860 for PE treatment  
2. see 73344

On procedure, see 75860 B. Mix polyol prior to reaction.

As polyol mixture is added to MDI, the reaction mixture turns red and suddenly turns hard. The reaction is quite exothermic.

B	Materials	Wt	Moles
	MDI	50.0g	0.2
	polyethylene glycol 400	36.0	.09
	glycerol EO	5.3	.01

React as in A above. As the amber isocyanate was mixed, the solution turned deep red (temp about 50°C). After 5 minutes the color turned back to amber. Only very slight thickening had occurred. The mixture was allowed to stand at room temp for 30 minutes. During this time it thickened to a viscous liquid and turned red again. Heated to 150°C to drive reaction to completion. Color turned to the reddish-brown which is normal for these MDI adducts. Reaction was repeated with same color changes being observed.

CONCLUSIONS 7/26 - Forms and filings from this adduct seem to be more flexible than those made from 75860 C.

It does not appear that the glycerol-EO adduct is tri-functional, but difunctional. More tests will be made.

7/27 - Forms made from this adduct appear to harder on aging so that after 48 hrs they are harder than those from 75860 C.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 75881

PROJECT Phosphate CompDATE Jan 15-17 1952PROJECT NO. D1-1004SIGNATURE Arthur L. Heiss

ABL-see 75880

Jan 15 Preparation of TDI-trial adducts terminating  
in OH groups.

A-	Material	Amt	Mols
	TDI	17.4 g	0.1
	glycerine*	18.4 g	0.2

\* dried according to NB 75880

mix at room temp. Immiscible - no reaction. Heat slowly with constant agitation. No reaction up to 100°C. Cool. Add pyridine catalyst. No reaction. Continue heating. Evolution of bubbles suddenly begins, and violent exothermic reaction develops. Not time to take temp. Some foaming. Product is an amber viscous liquid at 150°C, cooling to a sticky, resinous material.

B	Material	Amt	Mols
	TDI	5.2 g	.03
	glycerine-ED (90/10)	31.9 g	.06

mix at room temp. Mild exothermic reaction begins after 15-20 minutes. Heat to 150°C to complete reaction to completion. Product when cool is a thick, viscous, amber liquid.

This product has an altogether different structure than A or 75880, or any of the previous adducts. Instead of being a "creaky" liquid with a "long" nature, that is, with tendency to form long fine threads when being poured slowly, it is short, having a definite structure, being thick and gel-like in appearance. This is no doubt an indication that the molecules are not in the form of chains, but networks.

Jan 17 A. Apparently the calculated amount of TDI has not reacted - the product tends to foam. Perhaps only the primary OH groups react with TDI. This product is not water soluble.

## CONCLUSIONS

B - This product is water soluble and hygroscopic.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 75883

PROJECT Isocyanate CopolDATE Jan 15 - 1952PROJECT NO. 171-1054SIGNATURE Arthur L. Heiss

NICHOLSON &amp; SAWYER

ABT problem - evaluation of 75881-B

See discussion on 75880

Various ratios of 75881-B and 75876-A were weighed out and mixed under an atmosphere of dry nitrogen and allowed to cure at room temp under the same atmosphere. Contrary to expectations, the samples containing 75881-B began to foam immediately, and evidently some moisture was present in this product.

This will be repeated with another batch of 75881-B, this time taking more care to keep it product anhydrous.

The sample which served as a control and was 100% 75876-A did not foam under the same conditions, indicating that there was not enough moisture in the surrounding air to account for the reaction.

The series of samples was made with various AB cups containing 5 gram portions of the mixture of 75881-B and 75876-A. Amounts of the former varied in each sample were 0, 20, 40, 60, and 80% by weight.

At the end of 2 hrs cure at room temp, the 0% sample was unchanged. All the others had foamed, the firmness of the foam decreasing as the % of 75881-B increased. The 80% sample was quite sticky.

## CONCLUSIONS

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

Nº 75884

PROJECT Isocyanate ApplDATE Jan 17 1951PROJECT NO. 171-1004SIGNATURE Robert H. Weiss

HIGGINBOTHAM &amp; SAWYER

## Reactions of TDI with polyols -

It has been noticed (75881, 7339) that the pure ethylene glycol or glycerine react with diisocyanates less readily than some of the corresponding condensation products with ethylene glycol. It is possible, but not probable that this increased rate of reaction may be due to the fact that the isocyanate and polyglycol are more miscible as the mol wt of the latter increases. It is also possible that the reactivity of the terminal OH groups in the polyglycol become more reactive as they are separated from each other by the intervening chain. Still another possibility is that traces of the catalyst used in the EO condensation remain in the polyglycol and also catalyze the polyglycol-isocyanate addition. In the case of glycerine-EO condensates, mention must also be made of the fact that the condensates contain 3 primary OH groups, while glycerine contains 2 primary and 1 secondary. Primary OH reacts more vigorously with isocyanate than does secondary OH, according to the literature.

The catalyst used in the glycerine-EO condensation prepared by Hexion Process was 2% KOH. Two runs were made in which 3 mols of CP (undried) glycerine was reacted with 1 mol TDI. On one of the samples 2% of KOH was dissolved in the glycerine before addition of the TDI. The reactions were mixed at room temperature and allowed to stand for 1 hour. No sign of reaction in either case. Gradual heating was begun. The run containing KOH began to form a white solid material, that without KOH remained clear.

As the temp increased to 75°C, gas evolution began in both samples. As soon as the sample was removed from the hot plate, bubbling ceased. It was interesting to note, however, that after this bubbling reaction had been allowed to continue for 10-15 minutes the reaction mixture could be allowed to cool to as low as 65°C, and the gas evolution would continue at about the same rate. If the reaction mixture was allowed to remain at 75-90°C, the rate of gas evolution increased until it became quite violent.

## CONCLUSIONS

After reaction was complete, the sample containing KOH was a white solid, that without KOH is clear amber. The reaction was complete, the sample containing KOH was a white solid, that without KOH is clear amber. The reaction was complete, the sample containing KOH was a white solid, that without KOH is clear amber.

DEFENDANT'S EXHIBIT AB

Heiss Notebook - February 19, 1952 - May 2, 1952

Excerpts - Pages 79054  
79055  
79060  
79062  
79063  
79078 - 79080  
79083  
79084

Pages 961a to 970a

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 79054

PROJECT Monomale AnhydDATE Feb 20-17 1952PROJECT NO. DI-1004SIGNATURE Robert Weiss

See 79052

Effect of increased functional groups

In the following samples, the basic adduct of the TDI (2 mol) - PEG 400 (1 mol) adduct in which half of the PEG-400 has been replaced by an equivalent amount of another polyol with 3 or more OH groups. The resulting adduct was considered as a mixture of the following adducts:

50% adduct of 1 mol TDI and  $\frac{1}{2}$  mole PEG 40050% adduct of 1 mol TDI and  $\frac{1}{2}$  mole of polyol

Containing 1 OH groups.

These samples all prepared as 50% adducts in anhyd benzene and containing 5% by wt (based on adduct) of N-methylmorpholine salt.

No.	Name of polyol(X)	wt % OH	wt % of adduct 2 mol TDI 1/2 mol PEG 400 1/2 mol X	wt used to prepare 100g of adduct.		
				X	PEG 400	TDI
F	glycerine	57	579	5.3g	34.6g	60.1g
G	glycerine + 10 EO <sup>1</sup>	177	765	24.4	27.6	48.0
H	glycerine + 15 EO <sup>1</sup>	255	803	31.7	25.0	43.3
I	methanolamine	49.7	598	8.3	33.4	58.3
J	methanolamine + 3.0 EO <sup>1</sup>	93.7	642	14.6	31.2	54.2
K	methanolamine + 5.8 EO <sup>1</sup>	134.7	683	19.7	29.3	51.0
L	pentaerythritol	34	582	5.8	34.4	59.8
M	sorbitol	30.3	578	5.3	34.5	60.2
N	sucrose	30.2	578	5.3	34.5	60.2

<sup>1</sup> Prepared by Victor Kosmin at Central Research (Dayton)  
W B Sadowski - M Kosmin 10-17-51 etc.

NEXT PAGE



MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 79055

PROJECT Isocyanate prep.DATE Feb 20-27 1952PROJECT NO. 171-1004SIGNATURE Robert L. Weiss

Continued from 79054

Reactions F and I proceeded normally.

In reactions L, M, and N, the polyol did not dissolve in the PEG yw, even when some water was added to promote solution. This additional water was subsequently driven off with N<sub>2</sub> at 100-150°C, but the polyol remained as a fine dispersed solid. Reaction with TDI was attempted anyway. The solution remained turbid and considerable gelation as solid settled out on standing. It is not known at this time whether or not the polyol (either than PEG 400) reacted with the TDI.

Reactions G, H, J, and K were very violent, lowering the contents out of the bottles. These were repeated using half as much of the polyol (X) and a greater amount of PEG 400:

no	Name (X)	wt KOH	amount of adduct 2 mol TDI .75 mol PEG 400 1/2 mol X	X	wt used to repeat 100g of adduct. PEG 400	TDI
RF	glycerine	30.7	664	2.3g	45.2g	52.5g
RG	" + 10 ED	177	737	12.0	40.7	47.3
RH	" + 15.5 ED	255	716	16.4	38.7	49.9
RI	methanamine	49.7	673	3.7	44.7	51.6
RJ	" + 30 ED	93.7	695	6.7	43.2	50.1
RK	" + 5.8 ED	134.7	716	9.4	42.0	48.6

KG, RH, RJ, and RK were less violent than 79054 G, H, J, and K, but also still more vigorous than was normal. The violent ~~reactions~~ got hot enough to cause the benzene to boil and the mixture turned to a cloudy gel.

It is possible that the catalyst used in the prep. of these ED condensates is also catalyzing the TDI reaction. Efforts will be made to neutralize these ED condensates before drying them. Also, sodium acetate would be a better solvent than benzene.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

Nº 79060

PROJECT

Idea

DATE

March 4

1952

PROJECT NO.

SIGNATURE

Herbert Weiss

Reaction Products of Isocyanate and polyhydroxy compounds  
and/or their ethylene or propylene condensation

The reaction of various isocyanates with polyhydroxy compounds and/or their ethylene (or propylene) condensation results in a great number of interesting products depending on the reactants used.

Relevant notebook references involving basic ideas are:

73323 Sept 4, 1951

75869 Nov 30, 1951

73315 Sept 27, 1951

75876 Dec 26, 1951

73341 Oct 10, 1951

75879 Jan 14, 1952

75858 Nov 14, 1951

75887 Jan 28, 1952

75867 Nov 28, 1951

Although the original idea was to react 1 mol of a diisocyanate with each hydroxyl group of the polyol compound so that the resulting adduct would contain free  $-N=C=O$  groups, it is now believed that this ratio can be varied so that only some of the terminal groups are  $-N=C=O$ .

The advantage of having free  $-N=C=O$  groups in the adducts is that they are able to undergo normal isocyanate reactions (especially those with  $H_2O$ ) to form molecules of increased molecular weight. This makes them interesting as "self-curing" adhesives or surface-coatings. By adjusting the proportion of terminal groups in the adduct which are  $-N=C=O$ , it should be possible to obtain products which will cure to a great degree (where the ratio is high) to products which are "semi-curing" (where the ratio is low) and will act as their own plasticizing or toughening agents.

The materials which will react with isocyanates to form these adducts are given, as examples, as glycols, amines, ethanalamines, and various polyhydroxy compounds as glycerol, pentaerythritol, sorbitol, sugars, starches, etc. either alone or in mixtures with each other or their ethylene or propylene condensation products.

## CONCLUSIONS

These adducts should be useful in their cured form as adhesives, surface coatings, dielectrics, or (when fused) as insulating or structural materials.

Herbert Weiss  
March 4, 1952

Read and understood  
R. J. Gorman  
3/4/52

Read and understood  
William B. Bennett  
3/4/52

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 79062

PROJECT Isocyanate CondDATE March 5-6 1952PROJECT NO. 171-1004SIGNATURE Hubert H. Weiss

79055

March 5

In the belief that the alkalinity of the glycerine- and triethanolamine-EO condensates (due to KOH catalyst) may be affecting the rate of reaction of the condensate with isocyanate, attempts were made to remove the alkaline material:

1. Precipitation with  $\text{Co}_2$  - did not work - no prod.
2. Removal of  $\text{K}^+$  with ion exchange resin - did not work - evidently the potassium is not present in appreciably ionized form.
3. Neutralization with excess conc. HCl. The belief is that the water of neutralization and the excess HCl will be removed during the drying period.

A Condensate neutralized as in 3 above used to make a trial run according to the ratio of reactants used in 79055 RG; use same procedure as in 79055 RG

This reaction proceeded normally and was very easily controlled. In view of this another test run will be made using the full amount of EO condensate as in 79054 G.

A letter will be written to Walter Kerns at Dayton to find out what catalyst he uses. This same catalyst appears to be an excellent isocyanate catalyst.

March 6

B Reacted according to 79054 G - EXCEPT neutralize the EO condensate with excess HCl before the drying operation.

The reaction proceeds normally, upon the addition of the N-methylmorpholine catalyst (added in 1 ml portions) but was inhibited and the reaction did not get out of control.

## CONCLUSIONS

→ Certain EO condensates contain catalysts which also influence the subsequent -NCO reactions. These materials must be removed or neutralized in order to reduce viscosity of the -NCO reaction.

**MONSANTO CHEMICAL COMPANY. NO. 79063**  
PHOSPHATE DIVISION LABORATORIES

PROJECT Carboxylate CycleDATE 10/16/52PROJECT NO. 171-1004SIGNATURE Hubert G. Davis

See 79062 and 79054

Repeat 79054 series EXCEPT add excess HCl  
 to the ~~liquid~~ mixture before the drying process.

No.	Name of polyol(s)	wt per OH	amt mol out of adduct:		amt used to	
			2 mol TDF + mol PEG 400 + mol X	X	prepare 100% of adduct.	
					PEG 400	TDF
FN	glycerine	30.7	579	5.3	34.6 g	601 g
GN	glycerine + H <sub>2</sub> O HCl	177	725	244	276	480
HN	" + 15.580 HCl	255	803	31.7	25.0	43.3
IN	methanolamine	49.7	598	8.3	33.4	58.3
JN	" + 3.0 EO	93.7	642	14.6	31.2	54.2
KN	" + 5.8 EO	134.7	683	19.7	29.3	51.0

Since the methanolamine condensates are alkaline inherently and it was not possible to see when the catalyst was neutralized, 10 drops (about 0.4 grams) of conc HCl was added to each of the above in order to achieve this neutralization. IN formed a ppt, probably methanolamine hydrochloride, but it is hoped that this will decompose (at 150°C) during the drying operation. JN and KN remained clear.

The samples are heated at 140-150°C in the drying operation until a moist red paper held in the escaping gas stream does not indicate acid. During this process the ppt in IN disappears. This ppt reappears as the sample cools. It will be used anyway, since it will be interesting to note the effect of the HCl on the adhesive properties of the adduct, especially with urethas.

GN was cloudy when the benzene was added, but CONCLUSIONS changed no within 30 minutes as reaction was reached.  
 The crystals present in IN did not disappear during reaction.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 79078

PROJECT Isocyanate FoamDATE March 31 / April 10 52PROJECT NO. 171-1054SIGNATURE Herbert R. Davis

See 79077-

Due to D. J. that the prepared foams  
lead to failure, it will be interesting to  
determine the effect of increasing cross  
linking during curing. This will be in addition  
to increased rigidity obtained by decreasing  
molecular weight of the glycol. Cross linking should  
provide a different sort of rigidity.

Runs will be of the type 79074-C in which  
the ethylene glycol is replaced by an equivalent  
amount of polyhydroxy compound.

No.	Polyhydroxy Compound	cat. 100 OH	wt used per 100 grams of adduct.	Remarks
A	ethylene glycol	31	.42 grams	see 80958
B	glycerine	31	.42 "	
C	glycerine + 10 EO <sup>2</sup>	177	2.40 "	
D	glycerine + 15 EO <sup>2</sup>	255	3.45 "	
E <sup>2</sup>	methanolamine	50	.68 "	
F <sup>2</sup>	methanolamine + 3.0 EO <sup>2</sup>	94	1.27	
G <sup>2</sup>	methanolamine + 6.8 EO <sup>2</sup>	135	1.83 "	

<sup>2</sup> see 79054

<sup>2</sup> These reacted so rapidly that they were useless. Runs were  
repeated in which no N-methylmorpholine was added.

April 1.

All these foams collapsed on standing. In order of  
decreasing firmness, they are B and E, A, C and F, D and G.  
All samples suffered more shrinkage than A.

## CONCLUSIONS

Increasing cross linking during the foaming  
reaction does not have much effect on foam  
rigidity.

**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

No. 79079

PROJECT Isocyanate App.DATE April 1 1952PROJECT No. D1-1004SIGNATURE Habert Weiss

Effect of molecular wt of polyethylene glycol on foam properties.

Past work has shown that foams produced from the admixt. of 2 mols TDI and 1 mol polyethylene glycol are hard and brittle at PEG mol. wt 200 and rather soft at PEG mol. wt 400. The best foam should then be obtained (with TDI and a polyethylene glycol) when the average PEG mol. wt is somewhere between these two extremes.

No.	TDI	mols		Avg MW 1 adduct	wt used to prepare 100g adduct		
		PEG 200	PEG 400		TDI	PEG 200*	PEG 400*
A	2.0	1.00	0	548	63.5 g	36.5 g	0 g
B	"	.25	.25	598	58.2	25.1	16.7
C	"	.50	.50	648	53.7	15.4	30.9
D	"	.25	.75	698	49.9	7.2	42.9
E	"	0	1.00	748	46.5	0	53.5

The above adducts prepared by mixing reactants together in a bottle and letting stand at room temp. Reaction is exothermic.

\* tried by bubbling with dry  $N_2$  for 30 minutes at 110-150°C.

The final adducts varied in viscosity at room temp. from A which was a very thick liquid with little tendency to flow to E which was a viscous liquid which flowed readily. All are clear, amber products.

Foams will be produced from these on next page.

**CONCLUSIONS**

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No. 79080

PROJECT Osemyrate AmineDATE April 1-2 1952PROJECT NO. 121-1004SIGNATURE Herbert L. Harris

Foams from 79080

Due to fact that the above products have different molecular weights and that it is difficult to vary the small amounts of water and glycol used in the foaming reactions, the weight of the add-on used will be varied instead, as below, foams produced from following mix:

Additive	varied as below
Triton X-100	.056 grams 2 drops
N-methylmorpholine	.054 " 3 drops
water	.14 " 4 drops
ethylene glycol	.42 " 14 drops

Foam No.	Additive	wt. added	Remarks
A	79079 A	7.4 grams	Hard - difficult to mix
B	" B	8.0 "	Almost as hard as A
C	" C	8.7 "	Normal mixing properties
D	" D	9.3 "	like C
E	" E	10.0 "	like C

April 2 - after standing overnight, the above foams had following characteristics:

- A - Very brittle - easily crushed to a light, porous powder.
- B - A crisp, rigid foam. Some tendency to brittleness. Low strength.
- C - Stronger than B, still rigid. A, B, C have no shrinking tendencies.
- D - Softer than C. Some brittleness. Some shrinkage.
- E - Softest foam. Most shrinkage.

## CONCLUSIONS

79080 C - the best foam produced on this page, showed the approaching the maximum available using TDZ and polyethylene glycols. It is light and firm, but probably too weak to be useful as a structural material. It may still be useful for other purposes however. See 79082

PHOSPHATE DIVISION LABORATORIES

NO. 79085

PROJECT Organic CelluloseDATE Jan 22 1952PROJECT NO. 171-1034SIGNATURE H. L. H. H.

To investigate the possibility of getting better  
foams from more cross-linked adducts.

These adducts prepared by reacting a ratio of  
2 mols TDI, 1 mol PEG 400 and  $\frac{1}{3}$  mol of a triol (see below).

No.	Triol used when OH	Mol wt of adduct			wt used to prepare	
		2 mols TDI	1 mol PEG 400	$\frac{1}{3}$ mol triol	1 cop of adduct	
				trial	PEG 400	TDI
A	glycerine + 1080	177	725	24.4g	27.6g	48.0g
B	glycerine	31	579	5.4g	34.5g	60.1
Another sample prepared in which the glycerine content is half (on an equivalent basis) that in B						
C	glycerine	31	664	2.4g	45.2g	52.4g

Postponed because of more urgent work  
on Mason Reactor (AB2) and Synthesizer problems.



**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

**NO. 79084**
**PROJECT** *Isocyanate Temp*
**PROJECT NO.** *DI-1234*
**DATE** *April 3* **1952**
**SIGNATURE** *Herbert H. Harris*

Since the TDI-PEG foams do not seem to P.O. especially in standing, we will check a short amount of time on the TDI-PEG foams and see if this entire matter settles. See 79079 for TDI etc.

No.	MDI	Mols PEG 200	PEG 400	Ave MW of Adduct	Wt used to prepare MDI	Wt used to prepare PEG 200	Wt used to prepare PEG 400
A	2.0	1.00	0	700	71.5g	28.5g	—
B	"	0.75	.25	750	66.7	20.0	13.3g
C	"	0.50	.50	800	62.5	12.5	25.0
D	"	0.25	.75	850	58.8	5.9	35.3
E	"	0	1.00	900	55.6	—	44.4

**Procedure:** Weigh MDI into bottle and add glycol to molten MDI. Heat if necessary to keep molten. Mix well. Allow exothermic reaction to proceed.

All reactions proceeded smoothly to form brown, transparent films which increased in viscosity from A to E.

For combination of foams from 79084 C and D made the following best foam - density (see 79082)

Adduct (79084-C) 10.79grams  
 Triphenylamine .056 2 drops  
 N-methylmorpholine .054 3 drops

esters & acid varied as below

No.	Ratio	Exptl. Temp	Exptl. Temp	Exptl. Temp	Final Volume	Sp. Gr.	Remarks
AA	2g	60°C	0.00g	0.00g	135	.079	No shrinkage. Soft.
BB	2g	60°C	.21g	7.1	145	.074	2 times + than AA
CC	2g	60°C	.2g	14.1	90	.118	Best foam obtained
DD	2g	60°C	.2g	14.1	35	.306	Very hard
EE	2g	60°C	.2g	14.1	25	.428	Very hard

**BEST COPY AVAILABLE**

DEFENDANT'S EXHIBIT AC

Heiss Notebook - July 3, 1952 - November 10, 1952

Excerpts - Pages 84505  
84510 - 84511  
84519  
84526 - 84529  
84531

Pages 971a to 979a

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

MP 84505

PROJECT

Idea Sheet

DATE

July 8 1952

PROJECT NO.

SIGNATURE

Richard H. Weiss

## Solidification of Liquid Dielectric Materials...

On June 13, 1952 I sent the following note to EE Hardy:

"I noticed in your GE report that they are interested in converting liquid dielectrics to solids. You read that by reacting diisocyanates with polyols, etc. in such a ratio that the resulting product contains -OH as well as -NCO groups it is possible to cause 50% benzene solutions to gel to rather firm masses.

"Would there be any advantage in attempting to cause a liquid dielectric to solidify in this manner? Would this sort of mixture be able to compete with the polymerizable impregnants and offer a new field for liquid dielectrics?"

Dr. Hardy indicated that such products would be useful if the gel was stable and had good dielectric properties.

Subsequent work (NB 82338) June 16-17 1952 verified the above reasoning, and reaction of equimolecular quantities of TDI and dihydroxydichlorodiphenyl in Anisol 1248 medium resulted in the formation of a liquid which would "gel" to a hard, glassy solid on standing overnight at room temperature. The liquid-solid transition was reversible at about 70-80°C. The solid has a dielectric constant of 5.3.

On the basis of the above work it can be seen that liquid dielectrics can be solidified with the use of isocyanate-polyol reaction products, thus making them useful as capacitor impregnants, potting resins, and casting resins.

It is probable that a wide variety of dielectric solids can be obtained by proper selection of isocyanate, hydroxy compound, and liquid dielectric.

It is further possible that reaction of isocyanates with other active compounds such as amines, etc. will yield similar results.

## CONCLUSIONS

Read and understood  
William T. Lamm  
July 9, 1952

Read + understood  
James H. Seaver  
July 9, 1952

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 84510

PROJECT Isocyanate ApplDATE July 19, 1952PROJECT No. 171-1004SIGNATURE Robert E. Cull

MONSANTO &amp; SONS

## Summary of Aroclor-TEA-TDI reactions

NB Reference	Reagents			Products		Ratio	%	Variable	Resin
	Aroclor	TDI	TEA	Solid	Liquid	$\frac{\text{TDI}}{\text{TEA}}$	TDI+TEA		
82342 A	50.0g	38.9g	11.1g			3.0	50%		good
B	60	31.1	8.9			"	40	%	good
C	70	23.3	6.7			"	30	TDI+TEA	weak
D	80	15.6	4.4			"	20		weak
E	85	11.7	3.3			"	15		soft, weak
F	90	7.8	2.2			"	10		gel
G	95	3.9	1.1			"	5		gel
78976 H	50.0g	38.9g	11.1g			3.0	50%		good
A	addition of increased quantities of Aroclor to legend obtained from 78976 H.					"	45	%	good
B						"	40	TDI+TEA	good, soft
C						"	35		weak
D						"	30		"
E						"	25		"
F						"	20		gel
G						"	15		"
82344 A	50.0g	38.9g	1.0g			33	44%		
B	"	31.1	"			27	39	Decreasing TDI	
C	"	23.3	"			20	33		no
D	"	15.6	"			13	25		resins
E	"	11.7	"			10	20	Low TEA	formed
F	"	7.8	"			6.7	13		
G	"	3.9	"			3.3	8		
82345 A	50.0g	38.9g	11.1g	dark	↓ lighter	3.0	50%		good
B	"	31.1	"	the	color	2.4	46	Decreasing TDI	good, flexible
C	"	23.3	"	same		1.8	40		weak
D	"	15.6	"			1.2	35		weak
82343 A	"	0	"	none	↓	0	18	Low TEA	none formed
82345 E	50.0g	38.9g	11.1g		↓ decreasing	3.0	50%		good
F	"	"	8.3		color and	4.0	49	Decreasing TEA	good (flexible)
G	"	"	5.6		more	6.0	47		"
H	"	"	2.8			12.0	45		"
82344 A	"	"	1.0		↓	33.0	44	Low TDI	none
82343 A	"	"	0	none		∞	42		none

## CONCLUSIONS:

- I and II indicate that certain ratio of TDI+TEA must be maintained.
- III indicates that TEA definitely enters in reaction, even if more than catalytic amounts are present.
- II and III indicate that TEA conc. governs amount of resin formed, while TDI conc. governs molecular type of resin obtained.

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

No 84511

PROJECT Isocyanate Appl.DATE July 15, 1952PROJECT NO. 171-1004SIGNATURE Harold L. Smith

BROOKSTOWN &amp; SAWYER

Control from 84510

NB Reference	Reactants			Products		Ratio	%	Variable	Resin
	Aroclor	TDI	TEA	Solid	Liquid	mols TDI mols TEA	TDI+TEA		
78974A	50.0g	27.0g	23.0g			1.0	50%		spilled
B	"	31.8	18.2			1.5	"	TDI TEA ratio at constant TDI+TEA	good, flexible
C	"	35.0	15.0			2.0	"		good
D	"	37.2	12.8	max		2.5	"		"
E	"	38.9	11.1	↓ decreasing		3.0	"		"
F	"	41.2	8.8			4.0	"		"
G	"	42.7	7.3			5.0	"		"
H	"	43.8	6.2	↓ very little		6.0	"		"
I	"	45.7	4.3			9.0	"		"
J	"	46.7	3.3			12.0	"		"
K	"	47.3	2.7			15.0	"		weak
L	"	47.7	2.3			18.0	"		"

III indicates that the liquid phase is capable of forming resins through a wide range of  $\frac{\text{mols TDI}}{\text{mols TEA}}$  ratios at the ratio of  $\frac{\text{TDI+TEA}}{\text{Aroclor}}$  is kept above a certain

minimum. This would suggest that either there occurs a 3-way reaction involving Aroclor, TDI, and TEA, or that a certain proportion of a TDI-TEA reaction product is required to cause the Aroclor to solidify.

On basis of the thermal and solvent resistant characteristics of the resin (see 78977) it would seem that the first of the two suggestions is correct: the Aroclor is actually involved in some reaction with the TDI and/or TEA.

The following analytical data was obtained on 78977 series resins:

No	%C	%N	%Aroclor <sup>1</sup>	%TDI+TEA	%N in resin (calculated)
78974B	27.82%	5.43%	65.2%	34.8%	15.6%
" E	25.98	6.11	62.0	38.0	16.1
" G	25.29	6.41	60.3	39.7	16.1
" J	24.58	6.75	58.6	41.4	16.2
" L	25.61	6.65	61.3	38.7	17.2

**CONCLUSIONS**

<sup>1</sup> calculated from C/N content of resin (Aroclor 1242 is 92% C.)

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 84519

PROJECT Isoamylate ApplDATE Aug 7 1952PROJECT NO. DI-1004SIGNATURE Robert L. WeissTDI-TEA-Aroclor resin.

Past experiments (see 84510 for partial summary) have resulted in preparations of mixtures of a solid suspended in a liquid fraction. When TDI is added to the Aroclor-TEA mixture, reaction (as evidenced by temp increase and solid formation) occurs only during the early stages of the addition; after a certain point is reached, it seems that additional TDI is added without effect and remains in the liquid fraction as excess TDI.

Since the quantities of TDI and TEA used were calculated on the basis that 3 mols of TDI would react with 1 mol of TEA, it is apparent that some other reaction is taking place which uses less than this amount of TDI. One such possibility is that reaction is taking place to form an adduct of 2 mols-TEA and 1 mol TDI. It is believed at this time that the solid material is composed essentially of this adduct.

This can be checked by adding TDI to a TEA-Aroclor mixture until reaction ceases (as evidenced by the cessation of solid formation and the clearing up of the farred TEA-Aroclor dispersion) and noting how much TDI is consumed.

The mol wt of TEA is 149, but since commercial material contains approx. 15% diethanolamine, etc. as preservative, the true mol wt of such a mixture is about 142.

	mol wt	amt used	mols used
TDI	174	37.4 g	.214
TEA (mix)	142	55.5 g	.391
Aroclor	—	250.0 g	—

It can thus be seen that approx. 2 mols of TDI will react with 1 mol of TEA. This is in good agreement with the data of other experiments.

Robert L. Weiss

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 84526

PROJECT Isocyanate AnalDATE Aug 10 1951PROJECT NO. 171-1004SIGNATURE Robert J. Jones

TDI-TEA-Aroclor resins for 84522

Past work on these materials has indicated that the Aroclor probably does not enter into a chemical reaction with the TDI or TEA but is present as a dissolved inert impurity in some sort of very hard, high melting polymer formed by the TDI and TEA.

This is indicated by the fact that when the resin is heated in the absence of air, an oily liquid resembling Aroclor can be distilled from the solid, leaving behind a slightly charred, very brittle material.

If this intrapping of as much as an equal weight of an inert liquid by the TDI-TEA polymer proves to be the case, the entire system can have widespread applications. The process may be considered to be a new method for forming solid materials. Solid plastic products are currently formed by either allowing a solution of a resin to evaporate, by allowing a molten thermoplastic resin to cool, or by causing a thermosetting resin to polymerize.

It has been shown that Aroclor "solutions" of various TDI and MDI reaction products can be considered as types of thermoplastic (reversible) or thermosetting (irreversible) resins, according to the reagents used and the method of reaction. The reason that these materials may be considered unique from the standpoint of formation, is that the thermoplastic or thermosetting resin is removed in a dispense form. Where it is very unlikely, for instance, that the TDI-TEA polymer could ever be formed in a pure state and then combined with an equal weight of Aroclor to form a useful resin, this is easily done by heating TDI and TEA in the presence of Aroclor. Apparently, the polymer is formed in an extended lattice that remains retaining the Aroclor within itself.

## CONCLUSIONS

It is furthermore quite probable that these materials either than Aroclor or Polowax used are reversible. (next page)

Robert J. Jones  
William B. Bennett  
Aug 11, 1951

Read and understood,  
James H. Swales  
8/11/51

**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

No 84527

PROJECT Isosyrene CondDATE Aug 20 1952PROJECT NO. 171-104SIGNATURE John F. ...

Contd from 84526

Use of other non volatile liquids would result in the use of formation of resins that could be used as casting or potting materials in various electrical or mechanical applications. Proper choice of starting materials (isocyanates, active H compounds, inert liquids) would result in such qualities as good electrical properties, good fire resistance, good optical properties, good physical properties, etc.

Use of more volatile liquids could result in the formation of solid fuels (where the liquid is flammable) or imppt produce liquid weight, porous residues after evaporation of the liquid.

Read and understood  
 William D. Bennett  
 Aug. 21, 1952

Read & understood  
 James H. Saunders  
 8/21/52

CONCLUSIONS



**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

**NO 84528**
**PROJECT** Isocyanate Appl  
**PROJECT NO** 750.01-1004
**DATE** Sept 16 **1952**
**SIGNATURE** Robert F. Harris
**Tensile Properties of Thin Films made from TDI Adducts**

Adduct No.	TDI adduct of:	Yield Pt.	20 in. per min.		2 in. per min.	
			Elongation	Tensile	Elongation	Tensile
7957 D	toluene glycol	- PSI	0 %	5200-5600	0 %	4000-4200
7953 A	polyethylene glycol 200	-	0	3500-3700	0	2000
" B	" 400	1600 PSI	350-450	2600-3400		
" C	" 600	0	700-800	600-1100		
" E	" 1000	0	900-1100	200-400		
7957 B	" acet and cat 600 } mixture	0	900	600-1000		
" CC	" "	0	700-750	800-1000		
" DD	" "	0	900-1100	750-1000		
7954 F	PET 400 plus glycerine	-	0	4800-5100	0	9000-4200
7953 G	" " glycerine + 10 EO	2200-2400	230-390	3200-3700		
" H	" " glycerine + 15 EO	900	500-515	3500-3700		
7954 I	" " methanolamine	3200	175	3400-3600		
7956 O	" " ethylene glycol	2200-2600	375-500	4600-6000	275-450	4200-6000
" P	" " propylene glycol 1,2	4800-5200	0	6000+	375-475	6800-7400
" Q	" " butylene glycol 1,3	2400-2600	350-400	5300-5400	375-400	3800-4400
" R	" " butylene glycol 2,3	4800-5200	0	6000+	475	6000
" S	" " 2-methylpentanediol 2,4	-	0	6000+	0	4400
" T	" " 2-ethylhexanediol 1,3	5600	0	6000+	330-450	5600-5800
" U	" " adipic glycol	5200-6000	0	6000+	375	5200-6000
" V	" " glycerol- $\alpha$ -methyl ether	5600-6000	0	6000+	475-500	7200-7600
" W	" " glycerol- $\alpha$ -phenyl ether	4400-4800	0	6000+	400-550	5600-6600
8324 A	diethylene glycol dicarbonate 6	0	215-175	1800-2200		
" E	polyester (Ponyl # 152919)	0	600-800	2400-3200		
84514 A	Baker AA castor oil	1400-1600	115-275	1800-3600		
" B	" Palo #170 oil	2400	175-225	3400		
" C	" K oil	2400	125-200	2800-3600		
" D	" 400 oil	3200-3600	75-100	3200-3800	100	2800-3600
" E	" 900 T oil	3200	100	3100	100-150	2700-3100
" F	" XXX-1 oil	400	125	1400		
" G	" XXX-35 oil	1600	75	2800	50-75	2000-2500
" H	" XXX-310 oil	4000	50-75	2400-2900	75-100	2000-2400
" I	" XXX-317 oil	1200	50-75	2200-2400	50-60	1400-2000
" J	" Castor oil (hydrogenated castor oil)	2200	300-350	3400-3800	275-350	3200-3800
" K	" 2.0 percent 9		0	6000+	0	6400
<b>CONCLUSIONS</b>						
L	" Hexamethylenediol 11		0	6000+	0	6400
M	" Hexamethylenediol 13					

Centrifuge test results

MEDICATED CHEMICAL COMPANY  
PHOSPHATE DIVISION, LABORATORIES

No. 84529

SUBJECT Oscyanate ApplDATE Sept 19 1954PROJECT No. 752-1004SIGNATURE Herbert H. Weiss

Contd. from 84528

Ref. to 82310 for comparison with characteristics obtained by casual observation of films -

#### 1. Effect of distance between OH groups in the hydroxy compound.

noticed increase in elongation and decrease in tensile of the films as this distance increases in a dihydroxy compound (79053 A to E) and in a trihydroxy compound (79054 F; 79063 GN, H, V). Also compare effect of adding glycerol (79054 F) and methanalamine (79054 I). The latter gives greater elongation and a lower tensile.

Also note that the stress under which a film begins to stretch is inversely proportional to the distance between OH groups.

The above and the below observations pertain to series of adducts in which the constituents are similar and in which the major change concerns distance between OH groups only.

#### 2. Effect of side chains on OH compound when distance between OH groups is constant.

Note the series 79056 O, P, R, U, V, and W, all made with glycols in which the OH are on adjacent carbon atoms. Since these films are not very extensible, the values obtained at 2 in/min separation have the greater value. It can be seen that the stress required to cause a sample to stretch becomes greater as the complexity of the side chain increases. Surprisingly, no definite correlation is observed with regard to tensile and elongation.

#### CONCLUSIONS

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 84531

PROJECT Acrylonitrile (Tupac)  
3.0 - 7.1.01 - 52  
PROJECT NO. 750-01-1001  
HIGGINBOTHAM & SAWYERDATE Sept 19 19 52SIGNATURE John H. Jones

Sept 19 Special Sample for Sales. (Order 12885)

Since the attempts (NR 85133) to prepare an extended isocyanate adduct similar to Docmodur TH were unsuccessful, the adduct of 3 moles TDI and 1 mole of the condenser of 1 mole glycerine plus 6.6 moles propylene oxide will be prepared.

The below adduct prepared as usual as a catalyzed 50% benzene solution:

Material	Net wt	Adduct Net wt.	Net required to prepare 100g. adduct
A TDI	174	} 997	52.4g
glycerine 16.6 PO	475		47.6

\* NR 84729 Refr Index 8-5-52

Sept 12. exothermic reaction - no catalyst required. On standing over the weekend, this product changed to a clear transparent solid containing many fissures. This looks like a good way to solidify Acroclor.

B. Made the same as A. except replace benzene with 100 grams Acroclor 1412.

An exothermic reaction occurs. Bubbles are formed and the material sets up to a clear, tough solid. More flexible than the TDI-TDI-Acroclor reaction. Will not melt or burn when removed from flame.

C. Repeated B, but cooled during reaction to try to avoid bubble formation.

When the reaction is cooled, a clear, viscous yellow liquid results. A portion of this placed in an al. cup and held in a 100°C oven solidified in 5 minutes. Some bubbles were formed. Bubbles also formed during the solidification when the liquid was placed in a 50°C oven for 90 minutes, when it was treated with H-methyl morpholine and allowed to solidify at room temp.

## CONCLUSIONS

run temp controlled.  
D. Same as C except replace Acroclor with Indopol 100 (endoc polybutene). Incompatible - no prod.

DEFENDANT'S EXHIBIT AD

Heiss Notebook - January 16, 1953 - September 9, 1954

Excerpts - Pages 90101 - 90110

Pages 980a to 989a

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 90101

PROJECT Carbamate PolymersDATE Jan 6 1953PROJECT NO. 750-01-1080SIGNATURE [Signature]

Solidification of fluids with Carbamate Polymers  
Recent work will be of more general scope than that previously done on resins formed from Acrolein, triethanolamine, and TDI. The original work will be found on the following notebook pages:

82338-47, 82338-50  
84510-13, 84519-22, 84531  
78960-83, 78989-93, 78997-79000  
85101-3, 85105-7

The original purpose of this solidification is found on 82338, an idea sheet on 84505, and an extension of the original idea on 84526, 27.

Recent work is summarized below:  
Jan 6-9, 1953  
NB 89901-89907

Reaction of TDI with EO and PO condensates of glycerine and triethanolamine to form 50% solutions of adduct in Acrolein 1242. Many reactions too violent to handle. Addition of HCl to TDI modified reaction to where preparation of adduct solutions was easily accomplished. These adducts were clear liquids, unlike the liquid-solid mixtures obtained with TDI-TEA-Acrolein in 1952 work.

The adduct-Acrolein mixtures could be converted to solids by heating at various temperatures for varying amounts of time. Addition of small amounts of alkaline materials such as CaO and PbO decreased time needed to harden the solutions, but also seemed to favor bubble formation.

Some work was done on the polystyrene-urethane mixtures as developed by John K. Prueke at Santa Clara. These mixtures are lower melting than those prepared by Prueke (89908-9)

CONCLUSIONS

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 90102

PROJECT Condensate TestingDATE Jan 17 1953PROJECT NO. 750.21 1080SIGNATURE Robert H. Cross

HOBBSBOTHAM &amp; SAWYER

Jan 12-16, 1953  
MB 89908-12

50% Crocker 1242 solutions of the adducts of TDS and the EO and PO condensates. These are anhydrous and were prepared and condensed in vacuo. The freebase adducts cured too rapidly (15 min @ 100°C) and were filled with bubbles, even though HCl treated TDS was used. Further work with the TEA adducts must be postponed until we have a better idea of secondary activity and adduct curing.

The glycerine under 100% TDS adducts consisted of the Crocker to resin varying from rubbery to tough and brittle. Flexibility increased as the molal wt of the glycerine condensate increased. Cure times averaged from more than 5 hrs @ 100°C to 4-5 hrs @ 150°C.

Using the condensates of glycerine 3.1 PO and glycerine 13.2 PO, two series of adducts were prepared in which the Crocker 1242 content varied between 20 and 80% by weight. With 13.2 PO a series was obtained which varied from a soft gel to a tough, flexible product. With the 3.1 PO, the products were all hard and rather brittle. Those containing 65% and 80% Crocker tended to gel, indicating that these ratios were outside the limits of compatibility.

**CONCLUSIONS**

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 90103

PROJECT Monsanto ResinsDATE Jan 23 1953PROJECT NO. 750-01-1080SIGNATURE W. L. L. L. L.

Jan 19-23, 1953

NB 89913-23

Fluids other than Anoder 1200 were solidified using TDI and the condensation glycerin-13. LPO. All the Anoder were used as well as various other elastomers - type materials (see 89915). All sorts of materials are evidently suitable in this process, the principal limiting factor being that of compatibility.

Curing of resins was investigated in small glass vials & determining whether or not a large surface exposed to moisture influenced cure. It was found that typical hardening occurred in the vials (ie absence of atmospheric moisture).

Rate of cure decreased markedly as temp increased (NB 89919) but at temp over 150°C there was some bubbling. This may be CO<sub>2</sub> evolution from urethane groups as investigated by J. H. Saunders.

Addition of alkaline or acid-absorbing material to the liquid resin was tried in an attempt to decrease cure time. This was accomplished, but the tendency for bubble formation was also increased so that less satisfactory solids were obtained.

In order to obtain a rough idea of temp characteristics of these resins they were cooled to -120°C and heated to 200°C and 300°C on the Dresher-Johns MP apparatus. All samples tested were brittle at low temps, and were molten at 300°C, giving off Anoder vapor. At 200°C the resins were solid, but were somewhat softened and weakened.

A small amount of time was spent confirming that the same class lab synthetic way was easily fragmented into its components by melting and cooling. 89917

**CONCLUSIONS**

Most of the resins prepared in this way, esp. the more brittle ones, lack toughness. The softer resins suffer from what might be termed poor flow resistance. Possibly the use of MDI or other fluids (Castrol, GE 108 resin, etc) will improve the resins sufficiently.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 90104

PROJECT Isocyanate ResinsDATE Feb 2 1953PROJECT NO. 750-01-1080SIGNATURE William H. Hesse

Jan 26-30, 1953

NB 89924-29

Attempts to improve "heat resistance" of the resins by using other isocyanates and diisocyanates yielded no significant improvements. In general the MDI resins were more flexible than the corresponding TDI products.

Use of cumulated diols (GER-108 resin and castor oil) did not provide improved resins.

It was observed that it was possible to prepare castings free of bubbles at 110°C. Some shrinkage occurs, and when cure progresses in samples open to the air, a tough skin forms across the upper surface. This does not occur when cure takes place in closed containers.

It was observed that MDI could be deactivated by the addition of HCl gas the same as TDI. This will be investigated in more detail under job 1069, "Isocyanate Reactivity".

Some time was spent in manipulating the HCl content of lot 1167 TDI so as to adjust its activity. It would be desirable to do this in such a way that the TDI could be mixed with appropriate amounts of diol and alcohol and would then set up to a resin at room temperature. The HCl adjustment is very sensitive; however, work along this line will be continued.

**CONCLUSIONS**

Resins may be prepared free of bubbles. Exposure to moist air should be avoided in order to prevent the formation of a hard skin over the upper surface.



MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

Nº 90105

PROJECT Idea SheetDATE Feb 13 1953

PROJECT NO. \_\_\_\_\_

SIGNATURE Robert H. Hoes

Isocyanate resins as textile-treating agents.

I. Lathrop's Jan. 28, 1953 Technical Sales Report discusses various resin-treatments for textiles. These treatments serve a variety of purposes as providing water- or flame-resistance, reduced pilling, improved hand, etc.

It has been demonstrated in this lab. that glass cloth can be impregnated and/or laminated by using an isocyanate-urethane-urea resin. The specific material used was MB 89929 and was composed of 50% by wt Crocol 1242, 23% TDI and 27% of the condensate of 1 mole glycerol and 12 moles ethylene oxide. This material is a viscous liquid which, on heating, is transformed to a flexible, non-tacky polymer (presumably a polyurea-urethane plasticized by the Crocol).

The above is used as an example only. This idea deals with a similar process using other raw materials. For instance, it has also been demonstrated that many liquids sufficiently compatible with the isocyanate-urea adduct may be similarly solidified. It would thus appear that proper choice of starting materials should result in a product that could be used to treat conventional textiles and fabrics. This would be especially convenient for impregnating the fabric (or other porous material) with a rather non-volatile liquid and then fixing the liquid therein by polymerization of the polyurea-urethane.

As examples of fluids other than Crocol, mention is made of cumyl conventional plasticizer (which is sufficiently compatible with the isocyanate-urea adduct), and more specifically the types which have very low heat of solidification points so as to require a non-crystallizing or non-hardening treatment.

CONCLUSIONS

Read & understood  
James H. Saunders  
February 13, 1953

Read and understood  
Jean B. Bone  
February 13, 1953

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

Nº 90106

PROJECT Oxycarbonate ResinsDATE Feb 7 1953PROJECT NO. 250-01-1080SIGNATURE Robert H. JonesFeb 2-6, 1953

NB 89929

we move again - not much accomplished.

Becky Dugan being instructed by Tom Ford on determination of dielectric properties of solids so that experimental means may be evaluated.

CONCLUSIONS

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 90107

PROJECT Organic ResinsDATE Feb. 10 1953PROJECT NO. 750-01-1080SIGNATURE Robert E. Ross

Feb 9-13, 1953

NB 89930-3, 89935

Continued work on the adjustment of TDE  
Hcl content so as to permit solidification at room  
temperature has made great progress. The adjustment  
has ~~not~~ been found to be very delicate, and the  
rate of reaction appears to be influenced by the  
amount of exposed surface, i.e., contact with  
atmospheric moisture. Further work will be done  
using flat, loosely capped containers so as to  
exclude moisture during the solidification reaction.

Casting of resins for electrical testing and for  
use as display materials has demonstrated that  
there is much to be learned about the consistent  
preparation of bubble-free, uniform resins. The  
process as it stands at this time is unsuitable.  
For summaries of resins obtained see 89933 (and  
89941)

**CONCLUSIONS**

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 90108

PROJECT Phosphoric ResinsDATE Feb 24 1953PROJECT NO. 750-01-1080SIGNATURE Robert L. Ross

Feb 16 - 20, 1953  
NB 89934, 36-42

Tests on various resins (89934) indicated that they would burn when held in a gas flame but would not ~~remain~~ support combustion when removed. (One sample did have a tendency to remain ignited.)

Most of the time was spent in determining the dielectric constant and power loss on a series of six samples all cast from the same material. Power checks were obtained after a series of determinations were made using different techniques. It appeared that variations in results were due not so much to sample configuration as to sample composition.

Since all samples were cast from the same Anolon-acetone mixture, it seemed that the most likely source of difficulty was the curing of resins in cups. This permitted the surface material to react with atmospheric moisture, resulting in the formation of a resin of possibly different structure than that obtained from the curing of the bulk of the material in the absence of moisture.

#### CONCLUSIONS

The casting of resins in the absence of moisture will have to be investigated to see if more electrically uniform resins can be obtained.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

Nº 90109

PROJECT Glycerin EO ResinsDATE January 2 1953PROJECT NO. 50-01-1070SIGNATURE W. H. Davis

HISSEYMAN &amp; SAWYER

Feb 23-27, '53  
NB 89943-6

The original lot of glycerin EO condensate was used up and new material was obtained from Reel Bennett. This new lot had to be run with TDI containing various lots of H<sub>2</sub>O to determine the new water content.

The casting of bubble-free resins is still a serious problem. Materials reacted and cast under conditions as nearly anhydrous as it is practical to obtain (it dry box, dried containers, layer of oil over resin surface) still bubble when heated.

It is now suspected that this bubbling is not necessarily due to decarboxylation of the urethane, but may be caused by reaction of -NCO groups with traces of moisture in the condensate. One reason for believing this is that bubbling is often noticed when the original condensate-TDI reaction is run.

It is very difficult to remove all traces of moisture from these EO condensates. Attempts to do so have not provided bubble-free resins. Perhaps we will have to resort to crosslinking these products with materials more reactive than water, for instance ethylene diamine.

# CONCLUSIONS

Have not been able to obtain bubble-free resins.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 90110

PROJECT Decarboxylated ResinsDATE March 9 1953PROJECT NO. 750-01-1080SIGNATURE Herbert F. Gross

March 2-6, 1953

NB 89947-50

Attempts to reduce or prevent bubbling of resins during cure were continued.

It was thought that this bubbling might be due to moisture present in the OH compound. We have had indications that TDI or MDI react with alcohols before they react with water, and so it was possible that reaction of -OH groups with water occurred only at elevated temps (i.e. during the cure of the resin) resulting in CO<sub>2</sub> evolution. To test this, some of the glycerin-DEO condensate was dried with calcium hydride to remove all moisture. This material when reacted with TDI still bubbled. Either all the moisture was not removed (which is unlikely) or the gas was being formed by some other process (such as decarboxylation of the urethane).

It was recalled that some time ago, when melting points were obtained on isomers cured TDI and MDI products, the TDI films often bubbled as heating was continued past the melting point whereas the MDI adducts did not. This seemed to indicate that the MDI adducts were more stable. Because of this, an adduct was made at this time from MDI and the glycerin-DEO condensate which had been dried with calcium hydride. Bubbling occurred again.

## CONCLUSIONS

In view of the difficulties encountered in the preparation of bubble-free resins, this project will be discontinued in favor of others that promise to be of greater significance. It is felt that this particular problem is of relatively minor importance, and the work will be resumed when we have more data on isomer reactions.

DEFENDANT'S EXHIBIT AE

Billy R. Davis Notebook - January 6, 1953 - March 6, 1953

Pages 89901 - 89950

Pages 990a to 1040a

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 89901

A E

DATE Jan 6 1955

PROJECT ISOCYANATE RESINSSIGNATURE Billy R. Davis

PROJECT NO. \_\_\_\_\_

PREPARATION OF AROCLOR - TDI- TRIOL ADDUCTS

This is a continuation of previous work done on the solidification of Aroclor with TDI adducts.

An effort will be made to obtain a quick curing, clear, tough resin using Aroclor 1242, TDI and specially prepared triols. The triols to be used are Polyethylene and propylene oxide condensates of glycerin and triethanolamine prepared by Hulse & Jones.

The first trial used was glycerin with 6.6 mols of propylene oxide adduct.

mol ratio used:  
3 mols TDI / 1 mol trial

M.W. TDI	= 174
M.W. glycerin	= 92.09
M.W. P.O.	= 58.08
M.W. E.O.	= 44.05
M.W. TEA	= 149

$$\text{M.W. trial} = (92.1) + (6.6 \times 58.08) = 475$$

$$\text{THEOR M.W. adduct} = 475 + (3 \times 174) = 997$$

30 gram batch:

15 grams Aroclor 1242  
15 g TDI - trial adduct

$$\frac{3 \times 174}{997} = \frac{7 \text{ TDI}}{15}$$

$$\text{TDI} = 7.85 \text{ grams}$$

(TDI was added to a slurry of trial and Aroclor in a one-oz. bottle.)

$$\frac{475}{997} = \frac{7 \text{ trial}}{15}$$

$$\text{TRIOL} = \frac{7.15 \text{ gram}}{15.00 \text{ gram total adduct}}$$

Three ten gram samples of this product were placed in an oven at 146°C. One sample was untreated, one 1% lead oxide (PbO) added to one, and ca. 1% CaO added to the third.

(CONT. ON 89702)



MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 89902

PROJECT ISOCYANATE RESINSDATE Jan. 6 1953

PROJECT NO. \_\_\_\_\_

SIGNATURE Betty R. Davis

PREPARATION OF ARBCLOR - TDI - TRIOL ADDUCTS  
(CONT. FROM 89901)

The untreated sample required about one hour at  $140^{\circ}\text{C}$  to become a soft yel. It was removed from the oven after  $3\frac{1}{4}$  hours at  $140^{\circ}\text{C}$ . The film formed was very tough and rubbery. It was completely free of bubbles.

The sample treated with PBO required only 5 minutes (at  $140^{\circ}\text{C}$ ) to yel. It was removed after 16 minutes. The film formed was not clear. It contained many bubbles and was not as strong as the untreated sample above.

The sample treated with CaO required about  $\frac{1}{2}$  hour to yel. It was removed from the oven after  $1\frac{3}{4}$  hours at  $140^{\circ}\text{C}$ . It was similar to the sample treated with PBO above.

Adducts were prepared from other trial as follows:

TRIAL	THEOR. M.W. TRIOL	THEOR. M.W. ADDUCT	TDI, grams	TRIOL, grams	ARBCLOR, grams
A - GLY + 13.2 P.O. N.B. 84725	958	1380	5.67	9.33	15
B - GLY + 3.1 P.O. N.B. 84728	272	794	9.86	5.14	15
C - GLY + 3.0 E.O. N.B. 82939	224	746	10.5	4.5	15
D - GLY + 11.98 E.O. N.B. 82940	619	1141	6.86	8.14	15
E - TEA + 3.04 E.O. N.B. 82941	283	805	9.73	5.27	15
F - TEA + 9.19 E.O. N.B. 82943	553	1075	7.28	1.12	15

(CONT. ON 89903)

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 89903

PROJECT ASOCYANATE REINSDATE Jan 6 1953

PROJECT NO. \_\_\_\_\_

SIGNATURE Betty R. Davis

PREPARATION OF ARACLORE - TD1 - TRIOL ADDUCTS  
(CONT. FROM 89902)

<u>ADUCT</u>	<u>OBSERVATIONS</u>
89902-A	slight heat of reaction on mixing, product a clear liquid. A tough, rubbery, bubble free skin was formed on heating a 10 gram sample at 140°C for 4 hours.
89902-B	much heat liberated on mixing, solidified immediately
89902-C	much heat liberated on mixing, reaction product about half solid and half liquid
89902-D	very much heat liberated on mixing, reaction product completely solidified.
89902-E	much heat liberated on mixing, reaction product about 1/10 solid and 9/10 dark viscous liquid. A 10 gram sample in an alcohol dish required ca. 10 min. at 140°C to become hard, bubble filled skin.
89902-F	Very much heat liberated on mixing, reaction product completely solidified.

KOH was probably used as a catalyst in making the triols above and its presence would explain the high activity observed in adducts B, C, and D. No catalyst was used in making the triols used to prepare adducts E and F. However, the presence of excess TEA could be responsible for the high activity.

Adduct 89902-B was prepared again using low activity TD1 (high P61 contact) to determine if this would keep the reaction product from solidifying. Very little heat was liberated on mixing, the reaction product was a clear liquid. About 1% P60 was added to a 10 gram sample of the reaction product which was then heated at 140°C. About 1 1/2 - 1 3/4 hours was required for the sample to turn to a rubbery mass. (CONT. ON 89904)

TD1  
89460-A

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 89904

PROJECT ISOCYANATE RESINSDATE Jan. 7 1953

PROJECT NO. \_\_\_\_\_

SIGNATURE Billy R. Davis

PREPARATION OF TDI-ADDOLOR-TRIOX ADHESIVES  
(CONT. FROM 89903)

Adducts 89902-D and 89902-F were also reacted using TDI with high NCI content (88960-A). In both instances a clear liquid reaction product was obtained. Preparation of these two adducts using lot 1160 TDI (0.67% CI) gave a solid reaction product. Resins were prepared from the reaction products:

89902-F untreated - required ca 25-30 minutes at 140°C to harden. Resin was clear, tough, plastic, and contained a few large air bubbles.

89902-F with ca 1% CaO - required ca. 15-20 minutes to harden at 140°C. Resin was cloudy, tough, plastic containing many bubbles.

89902-D untreated - required 1 1/2 - 2 hours to harden at 140°C. Resin was very clear, completely bubble free, and plastic. It was softer and not as tough as 89902-F above.

89902-D with ca 1% CaO - required ca. 30 min. to harden. Resin was similar to 89902-D but was not clear due to CaO.

Another resin was prepared from adduct 89901. The first resin prepared from this adduct was completely bubble free (10 gram sample ca. 1 1/2 inch thick). A 1 inch resin was prepared by heating reaction product 89901 for 2 hours at 140°C. It was not bubble free as the first one. Like the first resin it was a plastic, gummy resin which readily reacted to the elimination stage after being deformed. A 1/2 inch resin was prepared from this adduct also contained bubbles.

(CONT. ON 89905)

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 89905

PROJECT ISOCYANATE REFINESDATE Jan 8 1953

PROJECT NO. \_\_\_\_\_

SIGNATURE Billy R. Davis

PREPARATION OF AROCLOZ - TDI - TRIOL ADDUCTS  
(CONT. FROM 89904)

Hydro. Cl in  
TDI-89905 = .23%  
O.C.D. 1-20-53

ADDITION OF HCl TO LOT 1160 TDI

A sample of lot 1160 TDI was deactivated  
by bubbling HCl gas through it. This sample was  
labeled TDI-89905.

The TDI above will be used to prepare  
arocloz - TDI - TRIOL adducts from those trials that  
give a solid reaction product with more active  
TDI. Also those trials (from the series prepared by Flores)  
not tested previously will be reacted with TDI in  
order to be sure that they ~~will~~ give a liquid  
reaction product with this TDI.

TRIAL	THEOR. M.W. TRIOL	THEOR. M.W. ADDUCT	ON BASIS OF 30 GRAMS		
			g TDI	g TRIOL	g AROCLOR
A - GLYCERIN + 9.0 P.O. N.O. 84722	614.6	1136.6	6.9	8.1	15
B - GLYCERIN + 2.1 P.O. N.O. 84728	272.1	794	9.86	5.14	15
C - GLYCERIN + 9.0 P.O. N.O. 82940	619.1	1141	6.86	8.14	15
D - GLYCERIN + 4.0 E.O. N.O. 82939	488.1	1010	7.75	7.25	15
E - GLYCERIN + 5.97 E.O. N.O. 82939	354.8	876.8	8.94	6.06	15
F - GLYCERIN + 3.0 E.O. N.O. 82939	229.1	746.1	10.5	4.5	15
G - GLYCERIN + 1.0 E.O. N.O. 82943	553	1075	7.28	7.72	15
H - GLYCERIN + 6.0 E.O. N.O. 82942	413	935	8.37	6.63	15
I - GLYCERIN + 7.0 E.O. N.O. 82941	282	805	7.73	5.27	15
J - GLYCERIN + 73.2 E.O. N.O. 84735	858.1	1380	5.67	7.33	15
K - GLYCERIN + 6.0 E.O. N.O. 84739	475	997	7.85	7.15	15

(CONT. ON 89906)

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 89906

PROJECT ISOCYANATE RESINSDATE Jan 9-19 1953PROJECT NO. 750.01-1080

SIGNATURE

Billy R. Davis

PREPARATION OF ADDUCTS FROM TDI-TRICLS-ARCCLOIR  
(CONT. FROM 89905)

## ADDUCT

## OBSERVATIONS

- 89905-A reaction product was a clear, viscous liquid.  
See N.B. 89910 for preparation of resin from reaction product.
- 1-19-53 - Adduct still a clear viscous liquid
- 89905-B reaction product was a cloudy, viscous liquid.  
See N.B. 89910 for preparation of resin.
- 1-19-53 - Adduct cloudy, viscous liquid
- 89905-C reaction product was a clear, viscous liquid.  
See N.B. 89910 for prep. of resin.
- 1-19-53 - Adduct still liquid
- 89905-D reaction product was a clear, viscous liquid.  
See N.B. 89910 for prep. of resin.
- 1-19-53 - Adduct still liquid
- 89905-E reaction product was a clear, viscous liquid. A thin layer of solid material formed on standing for ca 24 hours. See N.B. 89910 for prep. of resin.
- 1-19-53 - Adduct part liquid part solid
- 89905-F reaction product was clear, viscous liquid. As in 89905-E a thin layer of solid formed on standing 24 hours.  
See N.B. 89910 for prep. of resin.
- 1-19-53 - Adduct same as 24 hours after made
- 89905-G reaction product was viscous liquid.  
See N.B. 89910 for prep. of resin.
- 1-19-53 - Adduct still viscous liquid
- 89905-H reaction product was ca. 90% viscous liquid and ca. 10% soft solid material.  
See N.B. 89910 for prep. of resin.
- 1-19-53 - Same as when made
- 89905-I reaction product was viscous liquid.  
See N.B. 89910 for prep. of resin.
- 1-19-53 - Adduct same as when made
- 89905-J reaction product was clear liquid.  
See N.B. 89910 for prep. of resin.
- 1-19-53 - Adduct still clear
- 89905-K reaction product was clear.  
See N.B. 89910 for prep. of resin.
- 1-19-53 - Adduct same (CONT. ON 89907)

Billy R. Davis  
Jan 19, 1953

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

N° 89907

PROJECT ISOCYANATE RESINSDATE Jan 9 1952

PROJECT NO. \_\_\_\_\_

SIGNATURE Billy R. Davis

PREPARATION OF TDI-TRIDL-AROCLOX ADDUCTS  
(CONT. FROM 89906)

Adducts were prepared from glycerin and triethanolamine using TDI 89905, as before a 50% solution of adduct in Aroclor 1242 was used.

ADDUCT	TRIAL	M.W. TRIAL	M.W. ADDUCT	30 GRAMS BASIS		
				TDI	TRIDL	AROCLOX
89907-A	glycerin	92.1	64.1	12.77	2.23	15
89907-B	TEA	149	671	11.67	3.33	15

Adduct 89907-A did not react, that is, no heat was liberated on shaking the components in a bottle. Adduct 89907-B reacted giving a reaction product which was about 50% solid and 50% liquid.

The reactions above were repeated. This time the reactions were carried out in a beaker with vacuum agitation. The glycerin-TDI adduct was very slow to react and about 1% n-methylmorpholine was added. After addition of the catalyst the reaction proceeded very rapidly. The reaction product was a yellow, gummy, like wax. This reaction product was designated 89907-A1. A 1 gram sample was put in a jar even at 100°C. A very hard, bubble-filled resin resulted.

Reaction of TEA-TDI-Aroclor in a beaker with agitation gave a reaction product which was about 50% solid and 50% liquid as was experienced previously.

CONCLUSIONS

(CONT. ON 89910)

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 89908

PROJECT ISOCTANATE RESINSDATE Jan 12 1953PROJECT NO. 750.01 - 1080SIGNATURE Billy K Davis

**CARNAUBA WAX SUBSTITUTE**  
**PREPARATION OF POLYSTYRENE-PHENYL ISOCTANATE-LAURYL**  
**ALCOHOL WAX**

The purpose of this work is to further investigate the possibility of using phenyl isocyanate, polystyrene, and lauryl alcohol in the preparation of a wax substitute. Original observations concerning a wax from these materials were made by John K. Finche & Senten Clark. For a more complete history see letter from (1) J. H. Saunders to O. C. Jones, October 24, 1952 (2) John K. Finche to Dr. J. H. Saunders, November 3, 1952 and (3) Edgar E. Hardy to Mr. J. B. Fetter, January 5, 1953.

Using weights of materials suggested by Finche a wax was prepared from each of three polystyrene samples:

WAX DESIGNATION	POLYSTYRENE	WEIGHTS OF MATERIALS, GRAMS		
		POLYSTYRENE	Φ-NCO	LAURYL ALCOHOL
89908-A	LOW MOLECULAR WT. L-3 NBP 154640	10	50	78.4
89908-B	HIGH MOLECULAR WT. L-2500 USP 154460	10	50	78.4
89908-C	STYRENE-ACRYLO CO-POLYMER HIGH MOLECULAR WT. N.B. 154460	10	50	78.4

The samples above were prepared by dissolving the polystyrene in the Φ-NCO and then neutralizing the Φ-NCO with lauryl alcohol.

(CONT. ON 89909)

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 89909

PROJECT ISOCTANATE RESINSDATE Jan 13 1953PROJECT NO. 750.01-1080SIGNATURE Billy R. Davis

CARNAUBA WAX SUBSTITUTE  
(CONT. FROM 89908)

The temperature at which the waxy samples described on 89908 became soft were as follows:

<u>WAX</u>	<u>TEMP. °C</u>
89908-A	58-60°C
89908-B	58-60°C
89908-C	58-60°C
CARNAUBA WAX	70-73°C (53-88°C from literature)
4-NCO, LAURYL ALCOHOL REACTION PRODUCT	55-60°C

The above temperatures are not melting points but represent the temperatures at which the products become very soft.

This work will be continued later.

-53

See N.B. 89917



MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No. 89910

PROJECT ISOCYANATE RESINSDATE Jan 12-15 1953PROJECT NO. 750.01-KADSIGNATURE Billy R Davis

PREPARATION OF RESINS FROM ADDUCTS 89905 AND 89906											
TIME IN OVEN, HRS.	TIME REQUIRED FOR SAMPLING AND REMOVAL TO ANALYZE	TIME REQUIRED FOR PREPARATION OF FILM OVER TOP OF SAMPLE, HRS.	REMARKS	TYPE OF RESIN FORMED *							
68	25	75	89905-06 J 647 + 12.240	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							
68	25	75	89905-06 A 647 + 9.040	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							
68	25	75	89905-06 K 647 + 6.640	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							
68	25	75	89905-06 B 647 + 3.140	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							
68	25	75	89905-06 C 647 + 1.980	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							
68	25	75	89905-06 D 647 + 9.040	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							
68	25	75	89905-06 E 647 + 5.970	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							
68	25	75	89905-06 F 647 + 3.040	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							
68	25	75	89905-06 G TEA + 9.190	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							
68	25	75	89905-06 H TEA + 6.040	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							
68	25	75	89905-06 I TEA + 3.040	100% 125% 150% FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE FLEX., BUBBLE-FREE							

All the above resins were prepared using 10 g. of adduct in an aluminum foil cup. Attempts to obtain a 1" thick resin from adduct 89905-1 at 125-150°C were unsuccessful. For a better comparison see samples.

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

No 89911

PROJECT ISOCYANATE RESINSDATE Jan 14-15 1952PROJECT NO. 750.01-108DSIGNATURE Billy R. Davis

EFFECT OF VARYING THE AROCLOR CONTENT OF TDI-  
TRIOL - AROCLOR RESINS. (CONT. FROM 89910)

*The effect of varying the Aroclor content of resin was investigated briefly. Aroclor 1242 and TDI 89905 were used. The following adducts were prepared:*

ADDUCT	TRIOL	M.W. TRIOL	M.W. ADDUCT	WEIGHTS TDI	OF MATERIALS, GRAMS TRIOL AROCLOR	PER CENT AROCLOR
89911-A	GLYCERIN + 13.2 PD, N.B. 84735	858.1	1360	6.82	11.18 72.0	80
89911-B				11.9	19.6 58.5	65
89911-C				22.1	36.4 31.5	35
89911-D				27.2	44.8 18.0	20
89911-E	GLYCERIN + 3.1 PD N.B. 84728	272.1	794	11.85	6.15 72.0	80
89911-F				20.7	10.8 58.5	65
89911-G				38.5	20.0 31.5	35
89911-H				47.4	24.6 18.0	20

(CA. 4 HOURS) STATE OF ADDUCT, AT CA. 25°C  
IMMEDIATELY AFTER MIXING 4 DAYS AFTER MIXING

89911-A	clear, viscous liquid	same
B	" " "	"
C	" " "	"
D	" " "	extremely viscous liquid
E	cloudy, viscous liquid	same
F	" " "	"
G	very viscous, cloudy liquid	same
H	20% soft solid, 80% viscous, cloudy liquid	same

(CONT. ON 89912)

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

N<sup>o</sup> 89912PROJECT ISOCYANATE RESINSDATE Nov 16 1953PROJECT NO. 750.01 - 1080SIGNATURE Billy R. Davis

EFFECT OF VARYING THE AROCLOR CONTENT OF  
TDI-TRIDOL-AROCLOR RESINS (CONT. FROM 89911)

Resins were prepared from the amounts described  
on 89911. Ten gram samples were heated in  
an oven at 125°C. As before aluminum foil  
containers were used.

OBJECT	TIME REQUIRED FOR FORMATION OF FILM OVER TOP, HRS.	TOTAL TIME REQUIRED FOR SAMPLE TO GEL, HRS.	TOTAL TIME IN OVEN AT CA. 125°C, HRS.	TYPE OF RESIN FORMED *
89911-A	> 7 1/2	> 7 1/2	23	SOFT, BUBBLE-FREE GEL
89911-B	4 1/4	7 1/2	23	FLEXIBLE, WEAK, BUBBLE-FREE
89911-C	1 3/4	2 1/2	23	FLEXIBLE, BUBBLE-FREE FAIRLY STRONG
89911-D	1/2	2	23	FLEXIBLE, FEW BUBBLES, STRONG
89911-E	> 7 1/2	> 7 1/2	23	BRITTLE, WEAK, "LEAKS" AROCLOR, BUBBLE-FREE
89911-F	7 1/2	> 7 1/2	23	BRITTLE, BUBBLE-FREE, LEAKS AROCLOR
89911-G	2 1/2	4 1/4	23	BRITTLE, FEW BUBBLES, STRONG
89911-H	2 1/2	4 1/4	23	HARD, FEW BUBBLES

See samples for better comparison.

**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

No 89913

PROJECT ISOCYANATE RESINSDATE Jan 16-20 1953PROJECT NO. 750.01-1080SIGNATURE Billy R. Davis
USE OF VARIOUS AROCLORS IN PREPARATION OF TDI-  
TRIOL - AROCLOR RESINS

Other aroclors (than 1242) will be used in the preparation of adducts. TDI 89905 will be used to prepare all the adducts listed below:

TRIOL USED: glycerin + 13.2 P.O.  
 (A through J) N.B. 84735

ADDUCT	AROCLOR	WEIGHTS OF MATERIALS			STATE OF ADDUCT
		TDI, g.	TRIOL, g.	AROCLOR, g.	
89913-A	1148	5.67	9.33	15	dark liquid
-B	1221				clear, viscous liquid
-C	1232				" " "
-D	1248				" " "
-E	1254				" " "
-F	1260				Very viscous, clear liq.
-G	1268				not compatible
-H	4465				clear, extremely vis. liq.
-I	5442				clear, extremely vis. liq.
-J	5460				clear solid

TRIOL USED: glycerin + 3.1 P.O.  
 (K through S) N.B. 84728

89913-K	1148	9.86	5.14	15	dark, viscous, liq.
-L	1221				viscous liq.
-M	1232				" "
-N	1248				" "
-O	1254				Very viscous liq.
-P	1260				solid at 25°C
-Q	4465				solid at 25°C
-R	5442				solid at 25°C
-S	5460				solid at 25°C

Where aroclors higher than 1260 were used, they were mixed with melted aroclor and then TDI added.

(CONT. ON 89914)

**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

No 89914

PROJECT ISOCTANATE RESINSDATE Jan 20 1953PROJECT NO. 75D.01-1080SIGNATURE Billy R. Davis
 USE OF VARIOUS AROCLORS IN PREPARATION OF TRI-  
 TRIOL-AROCLORE RESINS (CONT. FROM 89913)

Resins were prepared from the adducts described  
 on N.B. 89913. In glass samples on aluminum  
 foil cups were heated in an oven at 125°C.

ADDUCT	TIME REQUIRED FOR FORMATION OF FILM OVER TOP, HRS.	TOTAL TIME REQUIRED FOR SAMPLE TO SET, HRS.	TOTAL TIME IN OVEN AT 125°C, HRS.	TYPE OF RESIN FORMED *
89913-A	3 1/2	> 6	13	DARK, FLEX, SOFT, BUBBLE-FREE
-B	1 1/2	2 1/2	13	FLEX, BUBBLE-FREE
-C	1	1 1/2	13	FLEX, BUBBLE-FREE
-D	1	1 1/2	13	FLEX, BUBBLE-FREE
-E	3 1/2	> 6	13	SOFT, FLEX, BUBBLE-FREE
-F	3 1/2	> 6	13	SOFT, FLEX, FEW BUBBLES
-G	0	0	13	NOT CLEAR, HARD, FLEX, BUBBLE-FREE
-H	1	1 1/2	13	HARD, FLEX, BUBBLE-FREE
-I	1 1/2	2 1/2	13	FLEX, BUBBLE-FREE
-J	1 1/2	2 1/2	13	BRIT., FEW BUBBLES
89913-K	5 1/4	> 7 1/2	23	DARK, FLEX, WEAK, BUBBLE-FREE
-L	> 7 1/2	none	23	FLEX, " "
-M	7 1/2	Hard	23	WEAK, FLEX, " "
-N	> 7 1/2	at	23	BRIT, " "
-O	> 7 1/2	4:30	23	BRIT, " "
-P	> 7 1/2		23	BRIT, " "
-Q	5 1/4		23	BRIT, " "
-R	5 1/4		23	BRIT, " "
-S	3		23	BRIT, " "

\* See sampler for better comparison

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**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

Nº 89915

PROJECT ACRYLATE RESINSDATE Jan 19-22 1953PROJECT NO. 250.01-1080SIGNATURE Billy R. Davis
USE OF PLASTICIZERS OTHER THAN AROCLOR IN  
PREPARATION OF RESINS

A series of adducts were prepared using plasticizer other than Aroclor. In all of these adducts (listed below) TDI 89905 was used. The trial used was a P.O. condensate of glycerin (13.2 P.O.).

5.67% plasticizer was used in all. Weights of materials were:

15.00 g. plasticizer  
 9.33 g. glycerin + 13.2 P.O. condensate  
 5.67 g. TDI 89905  
 30.00 g total

ADDUCT	PLASTICIZER	OBSERVATIONS, STATE OF ADDUCT
89915-A	HB 40	CLEAR, VISCOUS LIQUID
-B	THINOL 2L-109	NOT COMPATIBLE
-C	HYSTANER 4M 44-204-S	NOT COMPATIBLE AT ROOM TEMP, HEATED TO 125° - COMPATIBLE
-D	INAZO (CHLORINATED INDANO)	CLEAR, VISCOUS LIQUID
-E	PARAFLEX G-60 N.B. 64727	" " "
-F	TRICRE 674 PHOSPHATE	" " "
-G	SANTICIZER 141	" " "
-H	SANTICIZER 216	" " "
-I	DI-2-ETHYLHEXYL ADIPATE PHOSPHATE	PLASTICIZER REACTED WITH TDI - GAVE OFF LARGE AMOUNTS OF GAS! COMPATIBLE, LIQUID WHEN MIXED. SEDIMENTATION OCCURRED LATER
-J	DI-2-ETHYLHEXYL ADIPATE N.B. 74025-6	CLEAR, VISC., LIQUID
-K	POOREX-B BENZENE	NOT COMPATIBLE
-L	STERENE	CLOUDY LIQUID
-M	DIMETHOXY TRIMETHYLENE GLYCOL	CLEAR LIQUID
-N	DAV CORNING FLUID NO 200	NOT COMPATIBLE
	100% CTKS.	

(CONT. ON 89916)

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1005a

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

N<sup>o</sup> 89916SUBJECT ISOCYANATE RESINSDATE Jan 21 1953SUBJECT NO. 750.01-1080SIGNATURE Billy R. Davis

PREPARATION OF RESINS FROM ADDUCTS DESIGNATED ON  
N.B. 89915

Resins were prepared from the adducts described on N.B. 89915. Ten gram samples of each were heated in an aluminum foil cup in a 125°C oven. The adduct made from styrene was not heated in the oven but on a hot plate at ca 100°C for 5 hours.

ADDUCT	TIME REQUIRED FOR FORMATION OF FILM OVER TOP, HRS.	TOTAL TIME REQUIRED FOR SAMPLE TO GEL, HRS.	TOTAL TIME IN OVEN, HRS.	TYPE OF RESIN FORMED (FOR BETTER COMPARISON SEE SAMPLES)
89915A	6 1/2	> 6 1/2	22 1/2	FLEX., BLEEDS HARD
-B	1	2 1/2	22 1/2	HARD TOP, STICKY BOTTOM, FLEX
-C	1/2	1	22 1/2	STICKY, FEW BUBBLES
-D	2 1/2	3 1/2	22 1/2	FLEX., POOR TEAR RESISTANCE
-E	1/2	1	22 1/2	" " " "
-F	3 1/2	5 1/2	22 1/2	" " " "
-G	2 1/2	3	22 1/2	" " " "
-H	4 1/2	5 1/2	22 1/2	" " " "
-I	—	1/2	22 1/2	" " " "
-J	—	—	46	Liquid
-K	—	—	46	Liquid
-L	SEE ABOVE	—	—	SLIGHT. FLEX, BUBBLES, DROPPING
-M	2 1/2	> 2 1/2	18	FLEXIBLE, POOR TEAR RESISTANCE
-N	2 1/2	> 2 1/2	18	LIQUID

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

N<sup>o</sup> 89917OBJECT ISOCYANATE RESINSDATE Jan 20 1953OBJECT NO. 750.01 - 1080SIGNATURE B. H. R. Davis

## CARNAUBA WAX SUBSTITUTE

POLYSTYRENE - PHENYL ISOCYANATE - LAURYL ALCOHOL WAX

SEE N.B. 89908 AND 89909

## SOLIDIFICATION

Melting point determinations were run on the polystyrene - phenyl isocyanate - lauryl alcohol reaction products resulting in N.B. pages 89908 and 89909. These determinations were made by cooling a sample of each in a test tube and plotting temperature of the melt vs. time.

## SOLIDIFICATION

The ~~melting~~ <sup>solidification</sup> point of the  $\phi$ -NCO lauryl alcohol ~~reaction product~~ <sup>product</sup> found to be 56.5-57°C.

The products made from  $\phi$ -NCO, polystyrene, and lauryl alcohol were mixtures of polystyrene and the  $\phi$ -NCO - lauryl alcohol reaction product. All three products (89908-A, B, & C) gave two apparent ~~melting~~ <sup>solidification</sup> points. The first melting point was not at all sharp (polystyrene separated out). The second melting point of all three products was found to be about 57°C and was well defined.

Solid polystyrene started to form in the melt of product 89908-A at a temperature of ca. 76°C and in 89908-B at ca. 94°C. Product 89908-C was heated to 155°C and was still not a clear melt.



1007a

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 39918

OBJECT ISOCYANATE RESINS

DATE JAN. 21-23 1952

OBJECT NO. 7SD.01-1080

SIGNATURE Betty R. Davis

PREPARATION OF THICK, BUBBLE-FREE RESINS

In the use of resins or gels in transamers and condensers, bubbles or cracks would most likely be undesirable. In some instances, these resins or gels would have to be very thick. Efforts to obtain thick, bubble-free resins in that part here, for the most part, have been unsuccessful.

A series of samples were prepared and cured at various temperatures. The solvent used for this work had the following composition:

48.3g TDI  
56.7g GLYCERIN + 9.0 P.D. } TDI/TRIOLE = 3/1  
105.0g AUCORON 1242  
210.0g

The samples (B-6) were cast using small glass vials. Approximate dimensions of the resin were 1 1/2 inches high and 1/2 inch diameter. Sample 8918-A was cast in an aluminum foil cup for control (10g. of oil).

SAMPLE	APPROX. TIME REQUIRED TO GEL, HRS.	TOTAL TIME IN OVEN, HRS.	OBSERVATIONS, TYPE OF RESIN FORMED
<b>UNTREATED</b>			
125°C	71	24	CLEAR, FLEX, BUBBLE-FREE
150°C	71	22	" " " 1-2 SMALL BUBBLES
175°C	2 1/2	4	CLEAR, FLEX, BUBBLE FREE
200°C	2 3/4	3 3/4	MANY BUBBLES
<b>UNTREATED</b>			
125°C	71	24	CLEAR, BUBBLE-FREE, SLIGHT CRACK ON COOLING
150°C	71	22	" " " " " " " " " " " "
175°C	74	4	CLEAR, BUBBLE-FREE LIQ. WHILE HOT; GEL AT 25
200°C	2 3/4	3 3/4	" " " " " " " " " " " "

(CONT. ON 39919)

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 89919

PROJECT ACRYLAMIDE RESINSDATE Jan 21 - 23 1953PROJECT NO. 750.01-1090SIGNATURE Billy R. Davis

(CONT. FROM 89918)

SAMPLE	APPROX. TIME REQUIRED TO GEL, HRS	TOTAL TIME IN OVEN, HRS.	ORIGINATIONS, TYPE OF RESIN FORMED
<b>89918-C Ca 0.5% N-METHYL MORPHOLINE ADDED</b>			
125°C	>1	24	CLEAR, BUBBLE-FREE, SLIGHT CRACK ON COOLING
150°C	1	22	CLEAR, SMALL BUBBLES, " " " "
175°C	7/4	4	BUBBLES NEAR TOP & BOTTOM WHILE HOT, GEL AT 25°C
200°C	3 3/4	3 3/4	BUBBLE-FREE, LIQ WHILE HOT, GEL AT 25°C
<b>89918-D Ca 1% CaO ADDED</b>			
125°C	>1	24	CLOUDY, 1-2 SMALL BUBBLES NEAR BOTTOM
150°C	1	22	" " " " " " CRACK
175°C	1	4	CLOUDY, SMALL BUBBLES NEAR TOP AND BOTTOM
200°C	3/4	3 3/4	TOP SWOLLEN, BUBBLES, CRACKED ON COOLING
<b>89918-E Ca 1% P<sub>2</sub>O<sub>5</sub> ADDED</b>			
125°C	>1	24	CLOUDY, BUBBLE-FREE, CRACKED ON COOLING
150°C	1	22	" " BUBBLES NEAR BOTTOM, CRACKS ON COOL
175°C	1 1/2	4	TOP SWOLLEN, BUBBLES, CRACKS
200°C	3/4	3 3/4	" " " " " "
<b>89918-F Ca 1% ZnO ADDED</b>			
125°C	>1	24	CLOUDY, SEVERAL BUBBLES, CRACKED ON COOLING
150°C	1	22	" " FEW SMALL BUBBLES, " " " "
175°C	1/4	4	TOP SWOLLEN, BUBBLES, CRACKS
200°C	3/4	3 3/4	" " " " " "
<b>89918-G Ca 1% C<sub>2</sub>H<sub>2</sub> ADDED</b>			
125°C	>1	24	CLEAR, FEW SMALL BUBBLES, CRACKED ON COOLING
150°C	1	22	CLOUDY, " " " " " "
175°C	2	4	BUBBLES NEAR TOP AND BOTTOM
200°C	1 3/4	3 3/4	SWOLLEN AT TOP, MANY BUBBLES

addition of CaO, P<sub>2</sub>O<sub>5</sub>, ZnO, and C<sub>2</sub>H<sub>2</sub> increases the  
required to gel but greatly improves the  
quality of results.

B. R. Davis  
Jan 23, 1953

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 89920

OBJECT ISOCYANATE RESINSDATE Jan 22 1952OBJECT NO. 750.01-1080SIGNATURE Betty R. Danner

HIGH AND LOW TEMPERATURE CHARACTERISTICS OF  
AROCLORE-TRIC-701 RESINS

Samples of various resins were tested at  $-12^{\circ}\text{C}$  for 24 hours and then compared with the same resin at room temperature. The former resins were tested in the manner:

89911-D	20% Aroclor 1242	- 13.2 P.O. CONDENSATION
89905-J	50% " "	" " "
89911-A	80% " "	" " "

89911-H	20% Aroclor 1242	- 3.1 P.O. CONDENSATION
89905-B	50% " "	" " "
89911-E	80% " "	" " "

Samples 89911-H, 89905-B, and 89911-E were all brittle at room temperature. Samples 89911-D, 89905-J and 89911-A were not brittle at room temperature. At  $-12^{\circ}\text{C}$  all samples above were brittle with the exception of 89911-A which was a very soft gel at room temperature. Samples 89911-D and 89905-J were not as brittle at  $-12^{\circ}\text{C}$  as 89911-H, 89905-B, or 89911-E.

The dry resin alone and the following were tested at  $200^{\circ}\text{C}$  and  $200^{\circ}\text{C}$  on the Fisher melting point apparatus:

89913-H	50% Aroclor 4965	+ 13.2 P.O.
89913-J	50% Aroclor 5460	+ 13.2 P.O.
89913-R	50% Aroclor 5442	- 3.1 P.O.
89915-F	50% triaryl phosphate	+ 13.2 P.O.

All the resins were liquid at  $200^{\circ}\text{C}$  and extremely soft at  $300^{\circ}\text{C}$  and gave off vapor. At  $200^{\circ}\text{C}$  very little change in the nature of the resins was noted. Resins 89905-B and 89911-E had a slight tendency to solidify at this temperature. Resin 89911-H and 89913-R became somewhat softer and weaker.

(CONT. ON 89921)

1010a

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 89921

PROJECT ISOCYANATE RESINS

DATE Jan 22 1953

PROJECT NO. 7SD.01-1080

SIGNATURE

L. R. Davis

(CONT. FROM 89920)

The temperature characteristics of resins can be changed through use of more or less anclor or through use of different anclors (or other plasticizers).

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 89922

PROJECT ISOCTANATE RESINSDATE Jan 23 1953PROJECT NO. 750.01-1080SIGNATURE Billy R DavisADDITION OF HCl TO TDI

Any HCl was bubbled through a 1/2 gallon sample of TDI lot 1167. This TDI will be used for the preparation of resins. Hyd. Cl. content was 0.24%, analysis no. 30224.

The sample above was designated TDI 89922.

Feb 10, 1953

The hyd. Cl- content of lot 1167 TDI was 0.061 %

B. R. Davis

№ 89923

DATE Jan 23-26 1953

SIGNATURE Billy R Davis

adducts were prepared from some of the P.O. and E.O. Condensates of glycerin and TEA using MDI instead of TDI. Aroclor 1242 was used. Lots MD-11 and MD-12-D MDI were used. As before 3 mol of isocyanate was used for each mol of that. The following adducts were prepared:

ANALYT	TRIAL	M.W. TRIAL	M.W. ADJUST	30 g. BASIS		ADJUSTOR
				MO	TRIAL	
89923-A	13.2 P.O.-GLY	858.1	1608.9	7.0 (MO-11)	8.0	15
89923-B	6.6 P.O.-GLY	475	1225.8	9.2 (MO-11)	5.8	15
89923-C	3.1 P.O.-GLY	272.1	1022.9	11.0 (MO-11)	4.0	15
89923-C1	3.1 P.O.-GLY	272.1	1022.9	11.0 (MO-12-D)	4.0	15
89923-D	3.0 E.O.-GLY	224.1	974.9	11.6 (MO-12-D)	3.4	15
89923-E	3.04 E.O.-TEA	283	1033.8	10.9 (MO-12-D)	4.1	15

## OBSERVATIONS

85923-A very little hint of reaction; still a cloudy, very viscous liquid after standing 3 days.

89923-B reaction carried out in an aluminum foil cup,  
much heat liberated, at up immediately to  
a fairly strong red; resin contained small  
amounts and its resistance was not very good.

19923-C much land liberated, set up unarmored safely

" " " " set up immediately to give  
95% hard solid and 5% liquid.

March heat liberated, ca 70% soft solid and 10% liq.

Carbon 7 89925-C on an aluminum foil age gone a clay  
hard, brittle, almost bubble-free resin.

\* See A.D. 1885 for A.D. 1886

(CONT. ON 87928)

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

No 89924

PROJECT ISOCTANATE PGS/NSDATE Mar 26 1953PROJECT NO. 25001-1080SIGNATURE Billy R. Davis

(CONT. FROM 89923)

A small sample of MD-12-0 MDI was treated with HCl. The MDI was first melted and then the HCl gas bubbled through it. This MDI was used to prepare adducts corresponding to adducts 89923-C, 89923-D, and 89923-E described in N.B. 89923.

APART	COMPOSITION	OBSERVATIONS
89924-A	Same as 89923-C (with HCl treated MDI)	little or no heat liberated on mixing; adduct a cloudy viscous liquid at room temperature
89924-B	Same as 89923-D (with HCl treated MDI)	small amount of heat liberated on mixing; adduct about 90% viscous, cloudy liquid and 10% soft solid at room temp.
89924-C	Same as 89923-E (with HCl treated MDI)	much heat liberated on mixing; adduct almost thick enough to be considered a gel at room temperature.

See N.B. 89928 for preparation of resins from adducts 89924-A and 89924-B.

**CONCLUSIONS**

(CONT. ON 89927)

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

Nº 89925

PROJECT ISOCYANATE RESINSDATE Jan 26 1953PROJECT NO. 750.01-1000SIGNATURE Billy R Davis

- 1) TDI- CASTOR OIL - AROCLOR 1242 ADDUCT  
2) TDI- GENERAL ELECTRIC INTERMEDIATE R 108- AROCLOR 1242 ADDUCT

Adducts were prepared from Bedin's AA  
castor oil and General Electric R-108 coating  
intermediate, TDI 89905 and Aroclor 1242 were  
used to prepare both adducts

## 1) CASTOR OIL:

$$\begin{array}{rcl} \text{isocyanate equiv. (see N.B 84521)} & = & 386 \\ \text{M.W. TDI} & = & 174 \\ \hline \text{Theoretical M.W. of adduct} & = & 560 \end{array}$$

30 gram basis:

$$\begin{array}{rcl} 4.7 \text{ g TDI} & & \\ 15.0 \text{ g Aroclor 1242} & & \\ 10.3 \text{ g AA castor oil} & & \\ \hline 30.0 & & \end{array}$$

## 2) R-108 COATING INTERMEDIATES

$$\begin{array}{rcl} \text{Approx. M.W. R-108 intermediate} & = & 200 \\ 3 \times \text{M.W. TDI} = 3 \times 174 & = & 522 \\ \hline \text{Theoretical M.W. adduct} & = & 722 \end{array}$$

30 gram basis:

$$\begin{array}{rcl} 10.8 \text{ g TDI} & & \\ 15.0 \text{ g Aroclor 1242} & & \\ 4.2 \text{ g R-108 intermediate} & & \end{array}$$

## 3) Same as "2" above with no aroclor

30 gram basis:

$$\begin{array}{rcl} 21.6 \text{ g TDI} & & \\ 8.2 \text{ g R-108 intermediate} & & \end{array}$$

No heat was liberated on mixing the castor  
oil adduct. Much heat was liberated on  
mixing both 2 and 3 above. The castor oil  
adduct was a clear viscous liquid. The R-108 with  
aroclor (2) was a 10% solid and 90% dark liquid.  
The R-108 without aroclor (3) was completely solid  
gel.

(CONT. ON 89926)



MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

Nº 89926

PROJECT ISOCYANATE RESINSDATE Jan 28 1953PROJECT NO. 7SD,01-1080SIGNATURE Billy R Davis

(CONT. FROM 89925)

Resins were prepared from 89925-1 and 89925-2 adducts (10 g. samples in aluminum foil cups heated in oven at 125°C). Batch 89925-1 and 89925-2 requiring more than 24 hours at 125°C to gel. Both gave flexible, bubble-free, weak resins after 40 hours at 125°C.

A sample of 89925-2 treated with ca. 1% H<sub>2</sub>PO<sub>4</sub> (85%) gave a weak bubble-filled resin in about one hour at 125°C.



1017a

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

No 89928

PROJECT 15067 AMTE RESINSDATE Jan 28 1953PROJECT NO. 750.01-1000SIGNATURE Edly R. Hamer

(CONT. FROM 89927)

Resins were prepared from the series of adducts listed on 89927. The gram samples of all the adducts were heated at 125°C overnight (15 hours).

ADDUCT	TRIOLE	TYPE OF RESIN FORMED
89927-A	13.2 P.O. - GLY	CLEAR, FEW VERY SMALL BUBBLES, FLEX.
-B	9.0 P.O. - GLY	" " " " " "
-C	6.6 P.O. - GLY	CLEAR, MANY BUBBLES, FLEXIBLE
89927-A	3.11 P.O. - GLY	CLOUDY, FLEX, FEW SMALL BUBBLES
89927-D	11.98 E.O. - GLY	SEVERAL SMALL BUBBLES, FLEX.
-E	9.0 E.O. - GLY	FEW BUBBLES, FLEX, CLEAR
-F	5.97 E.O. - GLY	LARGE BUBBLES, STICKY
89927-B	3.0 E.O. - GLY	CLEAR, FLEX, WEAR, REQUIRED MORE THAN 24 HRS AT 125°C TO GEL - TOTAL TIME IN OVEN AT 125°C WAS 40 HRS.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No. 89929

PROJECT ISOLYANATE RESINSDATE Jan 28 - 16 1953PROJECT NO. 750.01-1090SIGNATURE Billy R. AdamsPREPARATION OF AROCLOR-TDI-TRIAL RESINS TO BE TESTED ELECTRICALLY

Comparison of TDI and TDI resins indicated that the physical properties of ~~the~~ resins were not greatly improved through use of TDI. If the resin prepared from the P.O. and E.C. condensates of glycerol, those made from TDI and the 11.98 E.C. glycerin condensate seemed to more nearly possess the desired qualities for a material to be used in condenser, transformer, etc. A large batch (900 g.) of this adduct was prepared and will be used to make resins whose electrical properties will be determined. Composition of the adduct was as follows:

205.8 grams TDI lot 1167-89922 (HCl added)  
 244.2 g 11.98 E.C. - GLYCERIN Condensate  
 450.0 g Aroclor 1242  
 900.0

Resins were prepared from this adduct in several forms. Six were prepared in the usual form that is, ten grams of adduct in an aluminum foil cup. These six samples were heated, kept the crush and at 110°C (total of 60 hrs) approximately. Dimensions of these resins were 2" by 1 1/2" by 1/2". They were completely bubble free, clear, flexible and reasonably tough.

Two other resins were cast from this adduct. One was cast in a 2 oz. wide-mouth bottle and the other in a metal adding tube. Dimensions of the resin cast in the 2 oz bottle were 1 3/4" high and 1 1/2" diameter. Dimensions of the adduct cast in the metal tube were 4 3/4" high by 1" diameter. Both were heated at 110°C for 85 hours. Both were clear and completely bubble-free. A hard "cap" was formed on the end of the resin cast in the metal tube (the end open to the air). The cap was used on the 2 oz. bottle, and the resin cured in absence of air. The cap was formed.

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 89930

PROJECT ISOCTANATE RESINS

DATE Feb 1953

PROJECT NO. 750.01-1080

SIGNATURE *Billy R. Davis*

CONTROL OF REACTION RATE OF ADUCTS BY ADJUSTING  
HYDROLYZABLE Cl CONTENT

An effort was made to obtain resins from ~~the~~ TDI-acroton 1242 - 11.98 E.C. *condensate* without having to heat it. This was done by adjusting the hyd. Cl content of the TDI used. The first series of reactions were carried out in aluminum foil cups. The Cl content of the TDI was varied by using a mixture of lot 1167 untreated and lot 1167 which had 0.54% hyd Cl (TDI-89922). Using a mixture of 47.4% TDI-89922 and 52.6% TDI-1167 a hard blueable-filled reaction product was obtained.

$$(474 \times .24) + (526 \times .061) = .1458\% \text{ hyd. Cl.}$$

using a mixture of ~~47.4~~ 47.5% TDI-89922 and 52.5% TDI-1167 a viscous liquid reaction product was obtained.

$$(475 \times .24) + (525 \times .061) = .1460\% \text{ hyd. Cl}$$

In reacting the same materials ~~shown~~ in 2 oz bottles (30 grams: 15g acroton, 15g a.d.s.c.f.) it was found that more than 50% acting TDI (lot 1167) was required to produce a hard resin whereas in the aluminum foil cups only 52.6% was required. Several reactions were carried out to determine why this was so. It is assumed that the difference was due to two factors (1) the degree of agitation used when mixing the reactants and (2) the degree of exposure to the atmosphere during reaction.

Samples prepared in 2 oz bottles using TDI containing 0.1451% hyd Cl required about two days to become solid.

A number of reactions were carried out in ~~closed~~ *one g. known bottles*. A plot of maximum temperature vs. per cent hyd Cl content of the TDI used was made.

(CONT ON 89930)

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 89930

ISOCYANATE RESINS

DATE Feb 1953

No 79,01-1080

SIGNATURE Billy R Davis

CONTROL OF REACTION RATE OF ADHESIVES BY ADJUSTING  
HYDROLYZABLE CL CONTENT

An effort was made to obtain resin without having to heat it. This was done by adjusting the hyd. cl content of the TDI. The first series of reactions was carried out in aluminum foil cups. The hyd. content of the TDI was varied by using mixtures of TDI-1167 untreated and lat 1167 which had 0.44% hyd. cl (TDI-89922). Using a mixture of 47.4% TDI-89922 and 52.6% TDI-1167 a hard, usable filled reaction product was obtained.

$$(47.4 \times .24) + (52.6 \times .061) = .1958\% \text{ hyd. cl.}$$

Using a mixture of 47.5% TDI-89922 and 52.5% TDI-1167 a viscous liquid reaction product was obtained.

$$(47.5 \times .24) + (52.5 \times .061) = .1460\% \text{ hyd. cl}$$

In reacting the same materials above in bottles (30 gms: 15g anhyd, 15g catalyst) cups found that more than 50% catalyst (lat 1167) was required to produce a hard reaction in the aluminum foil cups only 16% was required. Several reactions were carried out to determine why this was so. It was assumed that the difference was due to (1) the degree of agitation used under the reaction and (2) the degree of exposure to atmosphere during reaction.

Samples prepared in 2g bottles using TDI containing 0.1451% hyd. cl required about two days to become solid.

A number of reactions were carried out in 10g glass bottles. A plot of maximum temperature vs. per cent hyd. cl content of the TDI used was made.

(CONT ON 89930)

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

Nº 89931

PROJECT 18677NAT<sup>1</sup> RESINSDATE FEB 10 1953PROJECT NO. 760.01-1000SIGNATURE Billy R. Davis

(CONT FROM 89930)

The TDI used was a mixture of lot 1167 (.061% by wt cl.) and TDI-89922 (.24% by wt cl.). As in all the reactions on page 89930 the adducts were 50% alcohol 12+5 and 50% adduct.

Charge: TDI 9.15  
TRIOL 10.85  
ALCOHOL 20.00  
40.00

Lgt. of Cont<sup>1</sup> } .1433 .1398 .1415 .1424 .1429 .1432 .1433 .1434  
DI. 200 CONT<sup>1</sup> }

TIME, MIN	TEMP, °C	TEMP, °C	TEMP, °C	TEMP, °C	TEMP, °C	TEMP, °C	TEMP, °C	TEMP, °C	TEMP, °C
0									
2	50	35	38	38	41	42	41	37	38
4	110	43	60	46	54	51	57	48	46
6	112	49	80*	58	64	60	65	52	-
8	110	51	100	62	68	65	69	58	55
10	105	-	105	64	80*	68	83*	61	56
12	SUBS	50	100	-	85	72	85	62	58
14	FILLED	52	105	73	83	77*	83	63	58
16	SOLID	53	100	77	80	79	SOLID	64	58
18	-	-	-	74	SOLID	74	-	65	-
20	-	-	SUBS	SOLID	FEW	SOLID	-	65	57
22	50	-	FILLED	FEW	SUBS	FEW	-	-	59
24	40	-	SOLID	BUBBLES	-	DIAGNOSIS	-	60	-
								THICK GEL	

\* first noticed solid

Work on the above was discontinued because of a shortage of the F.O. Condensate.

See N.B. 89935 for a plot of maximum reaction temperature vs. lgt of Cont<sup>1</sup> of the TDI used.

(CONT ON 89935)

**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

No 89932

PROJECT ISOCYANATE RESINSDATE Feb 10 1962PROJECT NO. 2001-1000SIGNATURE Billy R. Davis
PREPARATION OF RESIN SAMPLES FOR  
R. L. JENKINS

Samples of the following adducts were prepared:

89932-A

37.5 g	Araclos 1242	} 25% Araclos TDI/TRIOL = 3/1
54.5 g	TDI 89922	
64.0 g	11.98 E.O. - glycerin condensate	
156.0 g	total	

89932-B

25.0 g	Araclos 1254	} 50% Araclos TDI/TRIOL = 3/1
34.3 g	TDI 89922	
40.7 g	11.98 E.O. - glycerin condensate	
100.0 g		

89932-C

75.0 g	Araclos 1260	} 50% Araclos TDI/TRIOL = 3/1
34.3 g	TDI 89922	
40.7 g	11.98 E.O. - glycerin condensate	
150.0 g		

89932-D

120.0 g	Araclos 4465	} 50% Araclos TDI/TRIOL = 3/1
74.6 g	13.2 P.O. - glycerin condensate	
45.4 g	TDI 89922	
240.0 g		

One or more samples of all the above were cast in the two following ways and cured at 110°C:

- (1) 1 1/2" high x 2 3/8" diameter tin cups
- (2) 3/8" high x 2 1/4" diameter aluminum foil cups

Samples of adduct 89927 were cast in the same manner.

(CONT ON 89933)



MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 89933

PROJECT ISOLYANATE RESINS 37 contDATE Feb 13-16 195PROJECT NO. 750.01-1090SIGNATURE Billy R Davis

(CONT. FROM 89932)

All of the samples cured in tin cans, bubbled near the top. About  $3/4$ " -  $1 1/4$ " all were bubble free near the bottom. Following is a summary of the resins prepared:

CODE	RESIN OR ADJECT	DIMENSION OF RESIN, IN.	CONTAINER IN WHICH CAST	CURING TIME AT 100° F, HRS	TYPE OF RESIN FORMED
89933-1	89929	$1 1/2$ " high x $2 7/8$ " DIA	TIN CAN	140	Top $1/2$ " full of bubbles, remainder clear, but gas, cracked on cool
-2	89932-A	$1 1/2$ " high x $2 3/8$ " DIA	TIN CAN	140	Bottom $7/8$ " clear and bubble free - top filled with bubbles
-3	89932-B	$1 1/2$ " high x $2 7/8$ " DIA	TIN CAN	140	Bottom $7/8$ " clear and completely bubble free - top filled with bubbles
-4	89932-C	$1 1/2$ " high x $2 7/8$ " DIA	TIN CAN	140	Bottom $3/4$ " bubble free, white - top full of bubbles
-5	89932-D	$1 1/2$ " high x $2 7/8$ " DIA	TIN CAN	98	Soft - Bottom $1/2$ " bubble free - top full of bubbles
-5A	89929	$7/8$ " high x $2 1/4$ " DIA	AL FOIL DISH	90	Clear, bubble free, clear, flexible
-6	89932-A	$1 1/2$ " high x $2 3/8$ " DIA	TIN CAN	115	Bottom 1" contained 3 small bubbles - clear top full of bubbles
-7	89932-A	$5/8$ " high x $2 1/4$ " DIA	AL FOIL DISH	115	Several bubbles near top
-7A	89932-A	$1/2$ " high x $2 1/4$ " DIA	AL FOIL DISH	85	Clear, one large bubble
-8	89932-B	$5/8$ " high x $2 1/4$ " DIA	AL FOIL DISH	115	Cloudy - few small bubbles near top
CONCLUSIONS	-8A	$5/8$ " high x $2 1/4$ " DIA	AL FOIL DISH	90	Clear, bubble free

\* See samples for better comparison

(CONT. ON 89934)

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

No 89

PROJECT ISOCYANATE RESINSDATE Feb 17PROJECT NO. 750.01-1080SIGNATURE Billy R. Davis

(CONT. FROM 89933)

CODE	RESIN OR ADJECT	DIMENSIONS OF RESIN, IN.	CONTAINER IN WHICH CAST	CURING TIME AT 110°C, HRS.	TYPE OF RESIN FORMED *
89933-4	89932-B	1 1/2" high X 2 3/8" dia	TIN CAN	115	top full of bubbles - bottom 1/8" bubble free cloudy, white

89933-10	89932-D	5" high X 1" dia	AL TUBE	140	flexible - filled bubbles
89933-11	89932-D	1/2" high X 1 1/4" dia	AL FOIL DISH	90	hard, clear, few fine bubbles

Small pieces of the resin were subjected to a flame test on which they were held in the flame of a burner until they were burning and then withdrawn. The following observations were made:

89933-1	Continued to burn after removal from flame
33-2	" " " " " "
-3	extinguished on removal from flame
-4	" " " " " "
-5	" " " " " "
-6	continued to burn after removal from flame
-7	" " " " " "
-8	" " " " " "
-9	extinguished on removal from flame
-10	" " " " " "

The three resins that continued to burn after removal from the flame were made from Croclay 1242 and were very hard. Resin (89933-5) made from 1242 and cured to a soft stage only did not continue to burn after removal from the flame. The hard resins made from higher Croclays (1254 and 1264) went out on removal from the flame.

**CONCLUSIONS**

\* See samples for comparison

(CONT ON 89941)

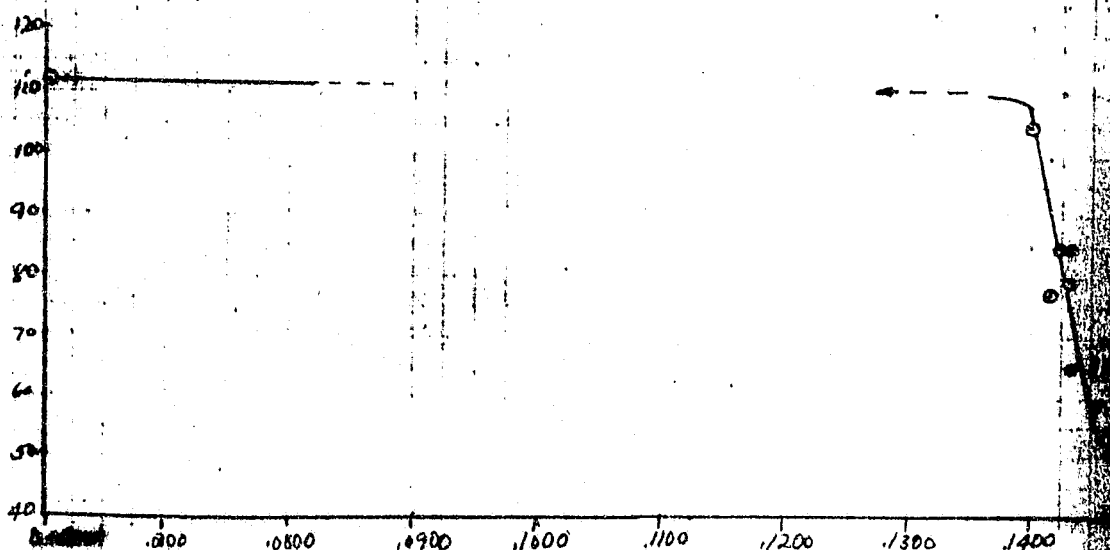
**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

Nº 89935

PROJECT: ISOCTANATE RESINSDATE Feb 12PROJECT NO. 750.01-1080SIGNATURE Billy R. Davis

(CONT FROM 89931)

Following is a plot of the data given on  
 P. 89931:



As can be seen the results are somewhat  
 inconsistent in the critical region. This inconsistency  
 could probably have been partly eliminated  
 by insulating the reaction bottle.

**CONCLUSIONS**

**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

Nº 89936

PROJECT ISOCTANATE RESINSDATE Feb 13-18 1953

PROJECT NO. \_\_\_\_\_

SIGNATURE Billy R. Davis
 DIELECTRIC CONSTANT AND DISSIPATION FACTOR  
 OF RESINS (2"Ø x 1/4" THICK) DESCRIBED  
 ON N.B. 89929

A tentative method of testing dielectric properties of Acetox-TDI-TRIS resins was suggested by [unclear] [unclear]. The method outlined by [unclear] with the necessary instrumentation for operation of the electrical testing equipment is repeat as follows:

Tentative Method for Testing Dielectric Properties of Solids Using Kohlrausch Solids-Cell

- 1) Sample should be cast in a disc, about 0.1" thick and at least 2" diameter, and of as uniform as possible thickness.
- 2) Measure the thickness with a micrometer. Try to get an average value over the whole area.
- 3) If surface is not already greasy or tacky, spread a thin layer of vasoline on surface. Press 2" flat discs on both faces. Place between plates of cell and lower the upper plate to contact.
- 4) Turn on oscillator, null detector and oscilloscope. Attach leads from bridge to cell, the insulated (hot) lead to the upper plate and the shield lead (ground) to the lower plate. Balance bridge, obtaining readings C and d.
- 5) Detach hot lead from upper plate, and let it hang in much air, if possible, within about 1/4" of the upper plate. Rebalance bridge, obtaining readings C' and d'.

**CONCLUSIONS**

(CONT ON 89937)

**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DESIGN LABORATORIES

No 89937

PROJECT ISOCYANATE REDIUSDATE Feb 13-19 1952PROJECT NO 28001-1080SIGNATURE Billy R. Davis

(CONT. FROM 89936)

1) Report this at every frequency for which data are desired.

2) Calculation of results:

$$C' - C = \Delta C$$

$$d - d' = \Delta d$$

$$\Delta C - C_e = C_x, \text{ the capacitance due to the sample}$$

For the present setup, with polyethylene support plates  $C_e = 5.8 \mu\mu f$

$$A_{eff} = \pi \left( r + \frac{t}{2} \right)^2$$

$r$  = radius of electrodes

$t$  = thickness of sample

$$\epsilon = \left( \frac{11.30 t}{A_{eff}} \right) C_x \text{ for measurements in cm.}$$

$$\epsilon = \left( \frac{4.45 t}{A_{eff}} \right) C_x \text{ for measurements in inches}$$

$$D = \frac{C_b}{C_x} \frac{f}{f_0} \Delta d = \text{Dissipation factor, DF}$$

=  $\tan \delta$ , where  $\delta$  = phase angle

$C_b$  is the balancing capacitor, plugged into the "Unknown Short" terminals.  
 Customarily here it is  $1000 \mu\mu f$ .  
 $f$  is the frequency of the oscillator  
 $f_0$  is the frequency setting of the "Range Selector" dial.

**CONCLUSIONS**

(CONT ON 89938)

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

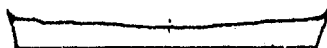
No 89937

PROJECT ACETATE RESINSDATE 4-13-18PROJECT NO. 75D.01-1080SIGNATURE Billy R. Davis

(CONT FROM 89937)

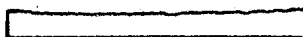
This expression for DF applies only for relatively high DF's, i.e. over 100% and then only with the polystyrene supports. For lower DF's the accuracy of this formula drops off, and a three term equation must be used.

The resins tested (after casting) were not of uniform thickness but were concave on one side as shown below:



CROSS SECTION

Before testing the resins were trimmed on the outside and top edges to give a sample that looked something like this:



To get a value for the average thickness of the sample five micrometer readings were taken and averaged. One measurement was made at the approximate center of the sample and the other four about 1/8" in from the outside edge and 90° apart:



For any one sample the value for average thickness could be duplicated (or redetermined) to  $\pm .004$ ".

(CONT. ON 89939)

CONCLUSIONS

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

No 89939

PROJECT 18OCTANATE RESINS

DATE Feb 13-18 1953

PROJECT NO. 750.01-1080

SIGNATURE Billy R. Davis

(CONT. FROM 89938)

Three samples of the resin (2" x 1/8") described on N.O. page 89938 were tested following the procedure outlined by Good. All three samples are of the same composition, some heated & adduct could were cured together. Values for their dielectric constants and dissipation factors were as follows:

SAMPLE	$\epsilon$	D.F., %
(1)	6.7	10.2
(2)	5.4	7.1
(3)	5.4	6.5

Since there was some variation in the results obtained, these same three resins were tested again the following day (2-18-53) after first removing the old foil and Vaseline and replacing ~~it~~ with new. The following values were obtained:

SAMPLE	$\epsilon$	D.F., %
(1)	6.8	10.2
(2)	5.5	7.5
(3)	5.4	6.6

These results check with those obtained the first time. Assuming that the properties of the three resins should be the same (since they are of the same composition, etc.), the results suggest that the technique may be faulty. It was thought that perhaps the greatest error would be due to the nonuniformity of the sample dimensions. After casting and before trimming the resin have a high ridge on the top edge:

**CONCLUSIONS**

In calculation of the average thickness it would make no difference whether the ridge was trimmed at level ① or level ②, however, it would make a considerable difference in the distance between the electrodes.

(CONT. ON 89940)

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 89940

PROJECT UREYANITE RESINS

3<sup>rd</sup> cont

DATE Feb 18 1953

PROJECT NO. 750.01-1080

SIGNATURE Billy R. Davis

(CONT. FROM 89939)

To determine just how the properties (E and D.F.) would be affected by the degree amount of trimming, a sample was tested after several stages of trimming. The resin tested was of the same sort as those three tested previously and described on N.B. 89939. The properties of this resin were determined (1) before any trimming was done (2) after trimming small amount off top edge (3) after trimming side and (4) after trimming more off the top edge. The following values were obtained:

SAMPLE (1)



(2)



(3)



(4)

E 3.7  
D.F. 5.13.7  
5.33.7  
5.34.2  
6.5

The four determinations above were made without using vasoline and foil on each side. Using foil and vasoline on (4) above gave the value of E was 5.6 and D.F. 7.7.

It was thought that more consistent results might be obtained by cutting a disc from the center of the resin samples since this would eliminate the edge ridge. Samples  $1\frac{1}{2}$ " in diameter were cut from sample (1), page 89939, and sample (4) above. Also,  $1\frac{1}{16}$ " diameter samples were cut from sample (3) and (2), page 89939 ~~and~~. These were then tested in the standard manner outlined by Head. The following results were obtained:

SAMPLE	E	D.F.	E	D.F.
	UNCORRECTED	UNCORRECTED	CORRECTED*	CORRECTED*
CONCLUSIONS (1) $1\frac{1}{2}$ " D	4.3	8.8	6.3	9.7
(4) $1\frac{1}{2}$ " D	3.6	7.4	5.5	8.2
(2) $1\frac{1}{16}$ " D	4.2	6.5	5.4	7.2
(3) $1\frac{1}{16}$ " D	4.1	6.2	5.3	6.6

(CONT. ON 89942)



**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

No 89941

PROJECT 150CT ANATE RESINS

DATE Feb 17 1953

PROJECT NO 250,01-1080

SIGNATURE Billy R. Downie

(CONT. FROM 89939)

Resins were prepared from some of the additives prepared last month and described on N.B. pages. 89905 and 89911. These were all cast in aluminum foil cups and heated for 90 hours at 110°C. The following resin were prepared: (all are 2" in diameter)

CODE	ADDUCT	THICKNESS OF BEHN, IN.	TYPE OF RESIN FORMED
89901-1	89905-A	<del>1/2</del>	clear, flexible, bubble-free
89901-2	89905-K	1/2	clear, flexible, bubble-free
89901-3	89905-B	1/2	cloudy, hard but not brittle, few bubbles
89901-4	89905-C	1/2	soft, flexible, clear, bubble-free
89901-5	89905-D	1/2	soft, clear, flexible, bubble-free
89901-6	89905-E	1/2	hard, cracked, glass cracks, bubbles, cloudy
89901-7	89905-F	1/4	hard, brittle, bubble-free
89901-8	89901-A	1/2	very soft gel, bubble-free, clear
89901-9	89911-B	1/2	soft, flexible, clear
89901-10	89911-C	1/2	flexible, clear, few small bubbles
89901-11	89911-D	1/2	hard, flexible, many bubbles

CONTINUED

**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

No 89942

PROJECT ISOCYANATE RESINS.DATE Feb 18PROJECT NO. 75D.01-1080SIGNATURE Billy R. Davis

(CONT FROM 89940)

\* The values obtained using samples less in diameter than the electrodes of the Baledough solid cell must be corrected, for the correction applied is as follows:

$$C_0 = \text{Capacitance due to air} = .2248 \frac{A}{t} \text{ (INCHES)}$$

where  $A$  = area between electrodes due to air

$$= \pi(1)^2 - \pi(\text{radius of sample})^2$$

$t$  = thickness of sample

Subtract  $C_0$  from the value of  $C_x$  obtained and use the ~~thickness~~ of the sample in calculation of  $\epsilon$

$$A_{EFF} = 3.14 \left( R + \frac{t}{2} \right) \text{ where } R = \text{radius of sample}$$

$$\epsilon_{CORRECTED} = \left( \frac{4.45 \times t}{A_{EFF}} \right) C_{CORRECTED}$$

$$D = \frac{1000}{C_{CORRECTED}} Ad$$

Elimination of the unevenness near the outside edge did not eliminate the large difference in value of  $\epsilon$  for sample (1) and the other three samples. The values of  $\epsilon$  for samples (2), (3), and (4) (both corrected and on 1.2" diameter sample) are in fair agreement. According to Had a wide variation in values of D.F. (for different samples of the same material) are not too uncommon.

**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

Nº 89943

PROJECT: ISOCYANATE REACTIONS

DATE: Feb 24-25 1953

PROJECT NO: 750.01-1080

SIGNATURE: Billy R. Davis

**REACTIVITY OF TDI WITH 12.0 MOLE E.O. CONDENSATE OF GLYCERIN**

A number of reactions were carried out to determine how much loss was present in a new lot of 12.0 mole ethylene oxide condensate of glycerin prepared by Bennett.

The 30 round bottles were used to carry out the reactions. A thermometer covered with aluminum foil was used to determine the reaction temperature. In all reactions the charge consisted of 50% anisole 1242 and 50% alcohol.

19.0 g anisole 1242  
 8.7 g TDI  
 10.3 g 12.0 mole E.O. condensate of glycerin  
 38.0 g total charge

The total was added to the anisole and mixed well by shaking. The TDI was then added and mixed. The bottle was immediately insulated with mica and temperature readings recorded every two minutes.

% hyd. cl. in TDI*	TEMP, °C											
	1148	1128	1055	0960	0720	0600	0570	0521	0570	0480	0442	
TIME, MIN	1466	1450	1398	1326	1147	1057	1013	1998	0990	0968	0940	
2	35	36	36	35	35	35	38	42	42	49	51	
4	40	40	40	39	40	40	47	52	55	63	65	
6	43	43	43	43	44	43	52	59	62	71	74	
8	45	45	45	45	46	46	57	63	66	78	88	
10	47	40	47	47	48	47	60	66	68	86	94	
12	48	48	48	48	49	48	62	66.5	69	88	92	
14	49	49	49	49	50	49	62	67	72	87		
16	50	49	50	50	50	49	62	67	72	84		
18	50	49	50	50	50.5	49.5	62	67	71			
20	50	49	50	50	50.5	50	62	66	70			
22	50		50	50	50.5	50						
CONCLUSIONS					50.5	49.5						

26 49.5  
 28 49  
 30

\* Top value based on hyd. cl. content of 89922  
 ally lower (bottom) value based on hyd. cl. content  
 of batch lot 1167 and 89922. Mixture of 89922  
 and lot 1167 were used to obtain final  
 hyd. cl. content of TDI used in reaction above  
 (PNT ON 89944)

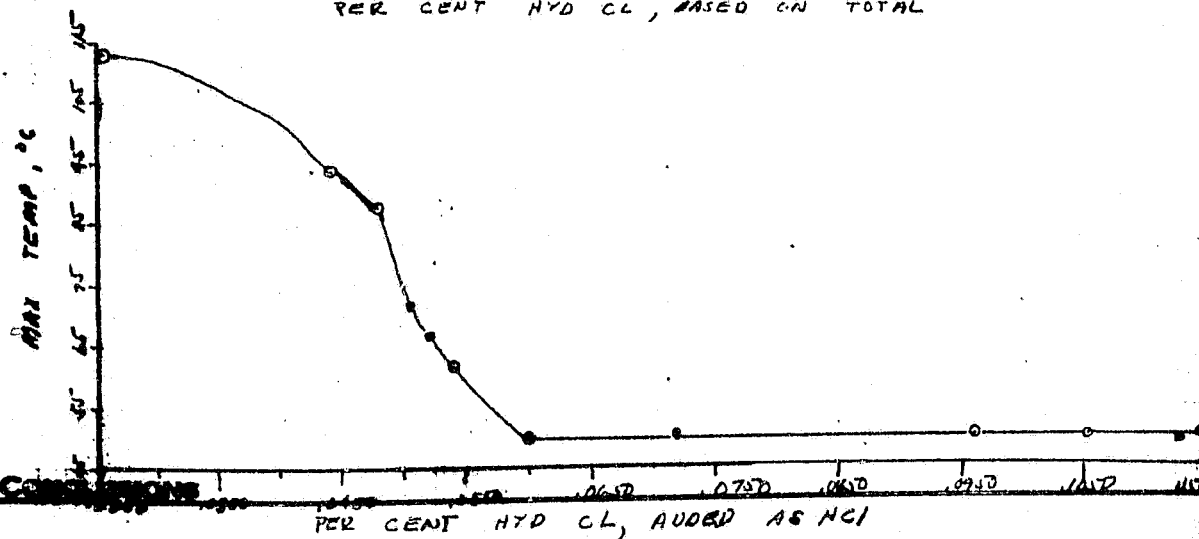
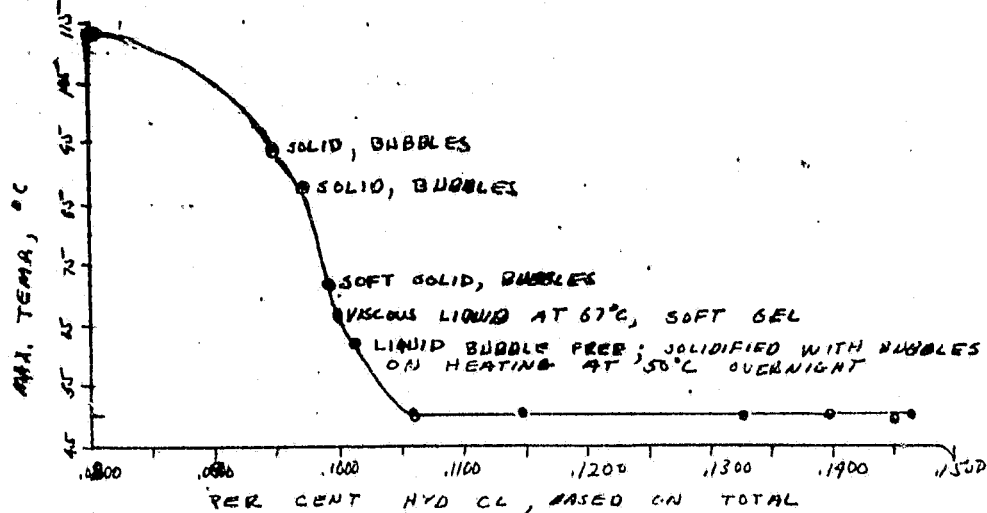
**MONSANTO CHEMICAL COMPANY**  
 PHOSPHATE DIVISION LABORATORIES

No 89944

PROJECT ISOCYANATE BEANSDATE Feb 24-25 1953PROJECT NO. 7901-1080SIGNATURE Billy R. Davis

(CONT. FROM 89943)

A reaction using unalloyed lot 1167 TDI (hyd cl = .481%) was so vigorous that the thermometer could not be placed in the beaker to record the temperature. Plots of hyd cl content vs. maximum reaction temperature are given below:



**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

No 89945

PROJECT ISOCYANATE RESINSDATE Feb 26-27 1953PROJECT NO. 750-01-1080SIGNATURE Billy R. Davis

PREPARATION OF ADDUCTS FROM 12.0 E.O. CONDENSATE OF GLYCERIN, ARACLO 1242, AND TDI

An effort will be made to obtain resins from the new batch of E.O. condensate of glycerin which will be bubble-free and require little curing time. Use will be made of the information on N.B. pages 89943 and 89944 to secure closely adjusted Cl content.

Three adducts were prepared from Araclo 1242, TDI, and the 12.0 mole E.O. condensate. All three were had the following composition:

50.0 g	Araclo 1242
27.1 g	12.0 mole E.O. condensate of glycerin
22.9 g	TDI
100.0 g	

The Cl content of the TDI used was as follows:  
(based on total hyp Cl content of lot 1167 and 89922)

ADDUCT	Cl, PER CENT
89946-A	0.1013
89946-B	0.1020
89946-C	0.1057

From the plot on page 89944 it can be seen that the balance values of Cl content are just large enough to prevent solidification on reacting.

Adduct 89946-A was very thick and contained some soft gel. Adduct 89946-B and C were liquid.

Mr. Mahman of Springfield mentioned that they had had trouble obtaining bubble-free gels at some and that a <sup>small</sup> layer of water oil dehydrating containing CONCLUSIONS would had helped prevent bubbling.

(CONT. ON 89946)

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

No 89946

PROJECT DOCTANATE RESINSDATE Feb 26-27 1953PROJECT NO. 750.01-1050SIGNATURE Billy R. Davis

(CONT. FROM 89945)

Resins were cast from the three adducts and a containing layer (ca. 1/8") of motor oil added. Two resins were prepared from each of the three adducts, one in a glass bottle and one in an aluminum foil cup. These were placed in an oven at 110°C. These resins prepared from 89946-A and 89946-B solidified in about 15 minutes but were full of bubbles. The resins prepared from adduct 89946-C required about 45 minutes to solidify. ~~There contained~~ These contained bubbles also but not as many as 89946-A and B.

The resins cast in the glass bottles were 2" x 1 1/2" diameter and those in aluminum foil cups 1 1/2" x 2" diameter.

Use of oil decreased the tendency of the resins to stick to the container in which they were cast. An adduct should with higher cl content should be prepared and a resin cast from it using oil (or some other incompatible liquid).

Some of the 12.0 E.O. condensate of glycerin was dried by heating to ca 150°C and then bubbling dry N<sub>2</sub> through. The three adducts above were then repeated using this dried condensate. Weighing of the materials was performed in a dry box (N<sub>2</sub> atmosphere). There were designated adducts 89946-A1, -B1, and C1. An additional adduct (89946-D) was prepared using TDI 89922 with a hyd. cl. content of 0.24%.

Adducts 89946-A1 and -B1 solidified on standing at room temperature and contained many bubbles. Both adducts 89946-C1 and 89946-D were remained liquid.

**CONCLUSIONS**

(CONT ON 89947)

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

No 89947

PROJECT ISOCYANATE RESINSDATE Feb 26-27 1953PROJECT NO. 750.01-1080SIGNATURE Billy R Davis

INSTRUCTIONS &amp; NOTES

(CONT. FROM 89946)

Heiss suggested that the lumps observed when the adduct were solidified at room temperature (was of low hyd cl TDI) were probably due to moisture. It was suggested that an adduct be prepared using TDI with low hyd. cl content to insure solidification at room temperature, and to coat the N-methylmorpholine would be added to remove any moisture present and the adduct cooled after mixing to keep it from solidifying before the catalyst could act.

An adduct (same composition as in 89945) was prepared using TDI with 0.6965% hyd cl based on total or 20486 % hyd cl based on HCl added. Two per cent (2 grams) N-methylmorpholine was added after the Anaclear, E.O. Condensate, and TDI had been mixed. The adduct was cooled in ice water immediately after addition of the N-methylmorpholine, however, it set up almost immediately. It contained many lumps. Better results would probably be obtained if the reaction had been carried out in a larger bottle so as to provide more surface area and better heat transfer. This adduct was designated 89947-A

March 2, 1953

An adduct was prepared from the 12.0 E.O. Condensate and TDI without using Anaclear. As in previous preparations the mole ratio of 12.0/1 that was used (the hyd cl content of 12.0 is 0.24%). Much heat was evolved in reacting and the material became considerably viscous. On reacting completely and cooling to room temperature the adduct became very viscous and sticky but did not solidify.

**CONCLUSIONS**

The gas evolved during reaction was passed through a  $\text{Ca(OH)}_2$  solution giving a precipitate.

(CONT. ON 89948)

**MONSANTO CHEMICAL CO.**  
PHOSPHATE DIVISION LABORATORIES

OBJECT ISOCYANATE RESINSDATE March 20 1953OBJECT NO. 750.01-1080SIGNATURE Billy R. Downer

(CONT FROM 89947)

A solution of 90% cresol 1242 and 10% ethylene diamine was prepared. The two were not compatible and separation occurred on standing.

Ten grams of the solution above was mixed with 10 grams of the cresol free adduct described on N.B. 89947. The two could not be readily mixed and the adduct solidified to a rubbery mass before all of the solution could be mixed in.

The use of a covering layer of liquid in casting of resins was investigated again briefly. Previous tests indicated (page 89946) that use of motor oil had some advantages.

An adduct was prepared from the 12.0 E.O. Condensate, TDI and cresol 1242. Isocyanate TDI (hydroxyl = 2.78) was used. Composition of this adduct was as given for adduct 89946-D.

Two resins were cast using this adduct. Two 9. gram bottles were used to cast the resins. Dimensions of the resin were  $1\frac{1}{2}$ " x  $1\frac{1}{2}$ " diameter.

One of the resins was covered with a  $\frac{1}{8}$ " layer of motor oil and the other with a  $\frac{1}{8}$ " layer of silicone oil. These were cured overnight (16 hrs.) at 125°C.

Both resins contained several bubbles. The one with which silicone oil was used had bubbles distributed throughout, whereas in the other the bubbles were more concentrated near the top.

#### CONCLUSIONS

Use of oil or other liquids during casting may reduce the number of surface bubbles but some CO<sub>2</sub> bubbles formed are trapped when the resins solidify.



**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

PROJECT ISOCYANATE RESINSDATE March 4 1951PROJECT NO. 75D.01-1080SIGNATURE Billy R Davis

PREPARATION OF ADDUCTS FROM COMPLETELY WATER FREE TRIOL

A sample of 12.0 mole E.O. condensate of glycerin was dried by adding  $\text{CaH}_2$  and ~~stirring~~ mixing. The mixture was heated at  $50^\circ\text{C}$  overnight to allow the  $\text{CO}_2$  to precipitate.

In previous reaction of TDI with the condensate it was found (N.B. 89947) that even with TDI of high hyd. cl. content  $\text{CO}_2$  was liberated. This was true even though the trial had been dried at  $150^\circ\text{C}$  by bubbling with  $\text{N}_2$ .

An adduct was prepared from the dried trial alone and sat 1167 TDI (active - .061% hyd. cl.). The TDI/condensate mole ratio was 3/1. Weighing of materials was performed in a dry box with an  $\text{N}_2$  atmosphere. The adduct solidified immediately on mixing. Many bubbles formed.

This adduct above was duplicated using inactive TDI (89922 - hyd. cl. = .24%). As before weighing was performed in a dry box. On mixing the adduct became hot and  $\text{CO}_2$  was liberated as in the adduct prepared previously from trial dried by heating at  $150^\circ\text{C}$ .

The  $\text{CO}_2$  ~~being~~ liberated must have been from the decomposition of the urethan rather than reaction of the isocyanate with water.

(CONT. ON 89950)

CONCLUSIONS

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 89950

CYANATE RESINS

DATE March 6 1953

750.01-1080

SIGNATURE Billy R Davis

(CONT. FROM 89949)

Resins were prepared from MDI and 12.0  
P.O. Condensate of glycerin. Condensate which  
had been dried with  $\text{CaH}_2$  was used.

A mole ratio of MDI/trial of  $\frac{3}{1}$  was used, the  
weights of reactants being:

16.4 g MD-12-D MDI  
13.6 g trial  
30.0 g

Weighing of reactants was performed in a  
dry box with an  $\text{N}_2$  atmosphere.

The adduct was prepared using pure lot MD-12-D  
MDI. The reaction was very exothermic and  
solidification occurred immediately. This adduct  
was a uniform, consistent, a solid amount of  
unsolidified liquid and the remainder a bubble filled, solid.

A second adduct was prepared using lot MD-12-D  
MDI which had been deactivated with HCl  
(N.B. 89934). The reaction was not exothermic  
as the one above. On standing at room temperature  
for several hours the reaction product solidified.  
It contained many bubbles.

CONCLUSIONS

DEFENDANT'S EXHIBIT AH

Flores Notebook pages 84728,  
84729,  
84732,  
84735  
August 1, 1952 - August 6, 1952

Pages 1041a to 1044a

1041a

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No 84728

PROJECT Oxide  
Alkylene Condensates  
PROJECT NO. 171-1017DATE Aug 1st 1952SIGNATURE Hector Hove

ROBERTSON &amp; SAWYER

Glycerine + 3 P.O.

Charge: 10.2-l. 3-neck r.b. flask

4 moles (368 g.) Glycerine, Merck Reagent  
8.2 (2%) KOH  
698 g. (12 moles) P.O. (placed 200 g P.O. in Fred funnel)

Data:

Time	Press cm. Hg	Temp °C	
8:45	0	140	started
9:00	2.5	145	
9:15	2.1	150	
9:50	1.8	164	
10:10	2.0	170	end

Flask gained 724 g. P.O. 3.1 P.O.

Added 100 cc H<sub>2</sub>O + shaken cov. in 10 min. pH  
of a 2% soln. was 6.8

Heated at 100°C under vac. for 2 hrs. Filtered

labeled Glycerine + 3.1 P.O.

Glycerine + 3.1 P.O.  
6/1/52

CONCLUSIONS

1042a

**MONSANTO CHEMICAL COMPANY**  
PHOSPHATE DIVISION LABORATORIES

No. 84729

PROJECT Alkylene Oxide Condensates DATE Aug. 2, 1952  
PROJECT NO. 171-1017 SIGNATURE Hector Florin

ENCLOSURE &amp; SAVER

Glycerine + 6.6 P.O.  
Charge in 2-l. flask  
2 mols (184 g) Glycerine  
4 g (2%) KOH  
880 g P.O. in funnel

## Data

Time	Temp. °C	Press. cm Hg	Remarks
10:30	130	30	started
10:45	145	30	
11:00	150	25	
11:30	155	20	
12:00	160	20	
12:30	160	16	
12:45	160	15	end

Flask gained 768 g P.O., i. 6.6 P.O.  
Added 100 cc H<sub>2</sub>O + blew in CO<sub>2</sub> for 10 min.  
Heated at 100°C under vac. for 2 hrs  
Filtered. Labeled: Glycerine + 6.6 P.O.

Mass spec No. 5  
Melt  
6/13/61

## CONCLUSIONS

1043a

MONROE CHEMICAL COMPANY 64732

PROJECT Alkylene Oxide CondensatesDATE Aug 5 1952PROJECT NO. 171-1012SIGNATURE Hector Flores

HIGGINS &amp; SAWYER

Glycerine + 9 P.O.Charge to 2-lb flask1.5 moles 138 g. Glycerine2.8 g. KOH850 g. P.O. in funnel

Data

Time	temp °C	Press. cm Hg	Remarks
9:00	140	20	started
9:15	151	22	
10:00	160	20	
10:50	160	22	
1:25	170	10	end

Flask gained 780 g P.O. i. 9 P.O.

Added 100 cc H<sub>2</sub>O. Blew in CO<sub>2</sub>.  
Dried & filtered.

Labeled Glycerine + 9 P.O.

Weiss Exp. No. 6  
 Malt  
 6/13/61

CONCLUSIONS

1044a

MONSANTO CHEMICAL COMPANY  
PHOSPHATE DIVISION LABORATORIES

No. 84735

PROJECT Alkylene Oxide CondensatesDATE Aug. 6, 1952PROJECT NO. 171-1017SIGNATURE Hector Flores

RECORDS/NAME &amp; SAWYER

Glycerine + <sup>13.2</sup> P.O.  
 Charge: (In a 2-l. flask)  
 one mole (92.9) Glycerine  
 29 KOH (24.8)  
 + ~~100~~ 8 P.O. in funnel

Data			
Time	Temp.	Press	Remarks
	°C	cm Hg	
10:30	150	20	started
11:00	165	15	
11:30	165	20	
12:00	152	18	
1:00	160	22	
2:00	160	24	
2:15	165	20	end

Flask gained <sup>768</sup> 270 g : 13.2 P.O.  
 Added 100 cc water (cloudy, on border of solubility)  
 + 100 cc CO<sub>2</sub> for 10 min. (pH 2.0)  
 Evaporated water under vac. 1" Hg

Labeled: Glycerine + 13.2 P.O.

This product + those of NB 24728, 24729 + 84732  
 were turned in to U.S. Bureau (a quart of  
 each)

Wells Exp. No. 6

Wells

6/13/61

CONCLUSIONS

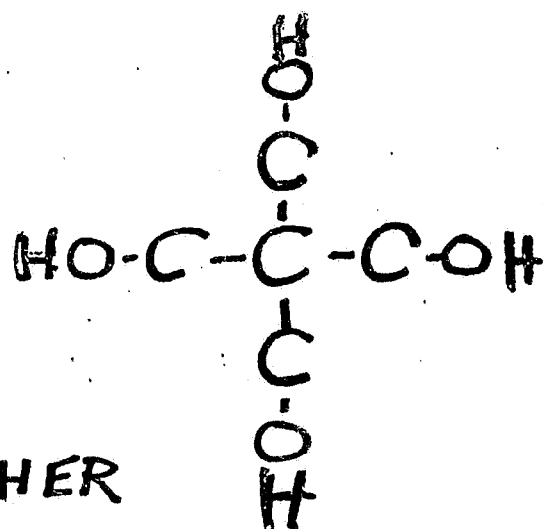
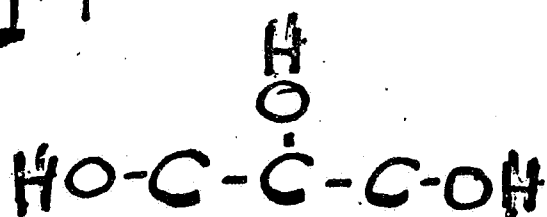
DEFENDANT'S EXHIBIT AJ-1 - AJ-6

CHARTS

Pages 1045a to 1050a



AJ-1



POLYOLS - NOT POLYETHER

(WILL CROSS-LINK)

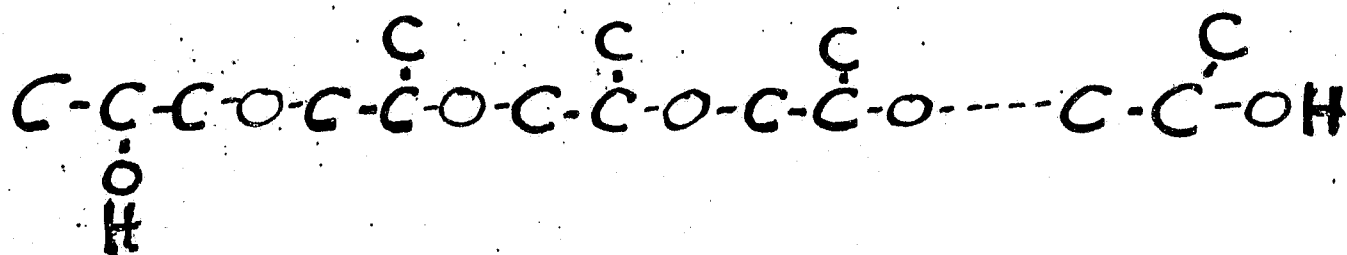
(prim.)



DIOL - NOT POLYETHER

(WILL NOT CROSS-LINK)

(prim.)



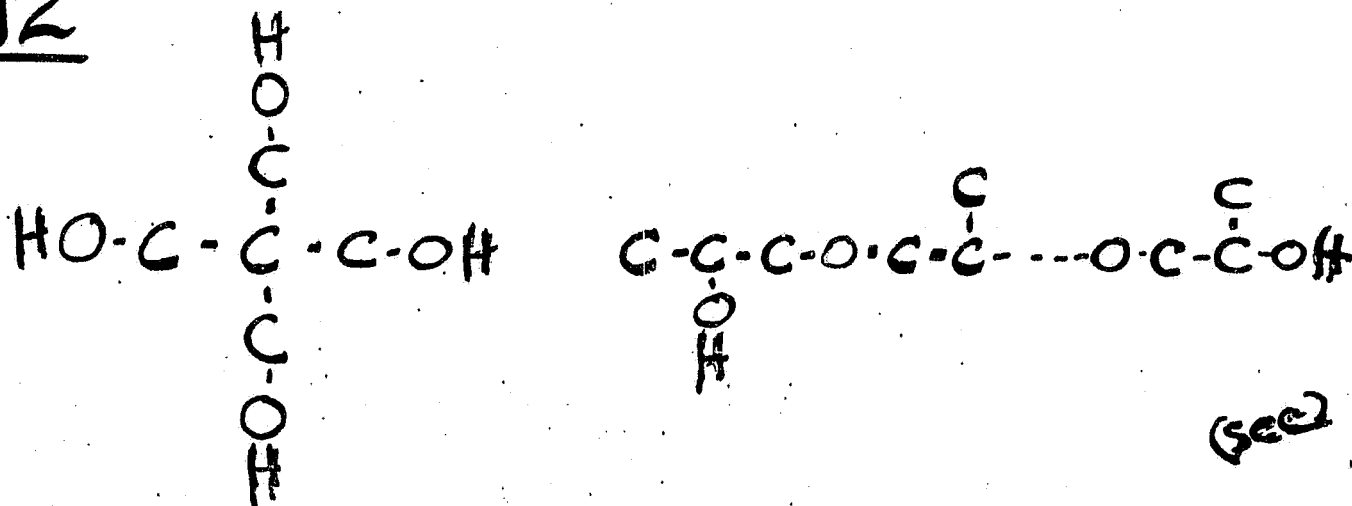
POLYETHER DIOL (PROPYLENE OXIDE POLYMER)

(WILL NOT CROSS-LINK)

(sec.)

AJ-2

1046a

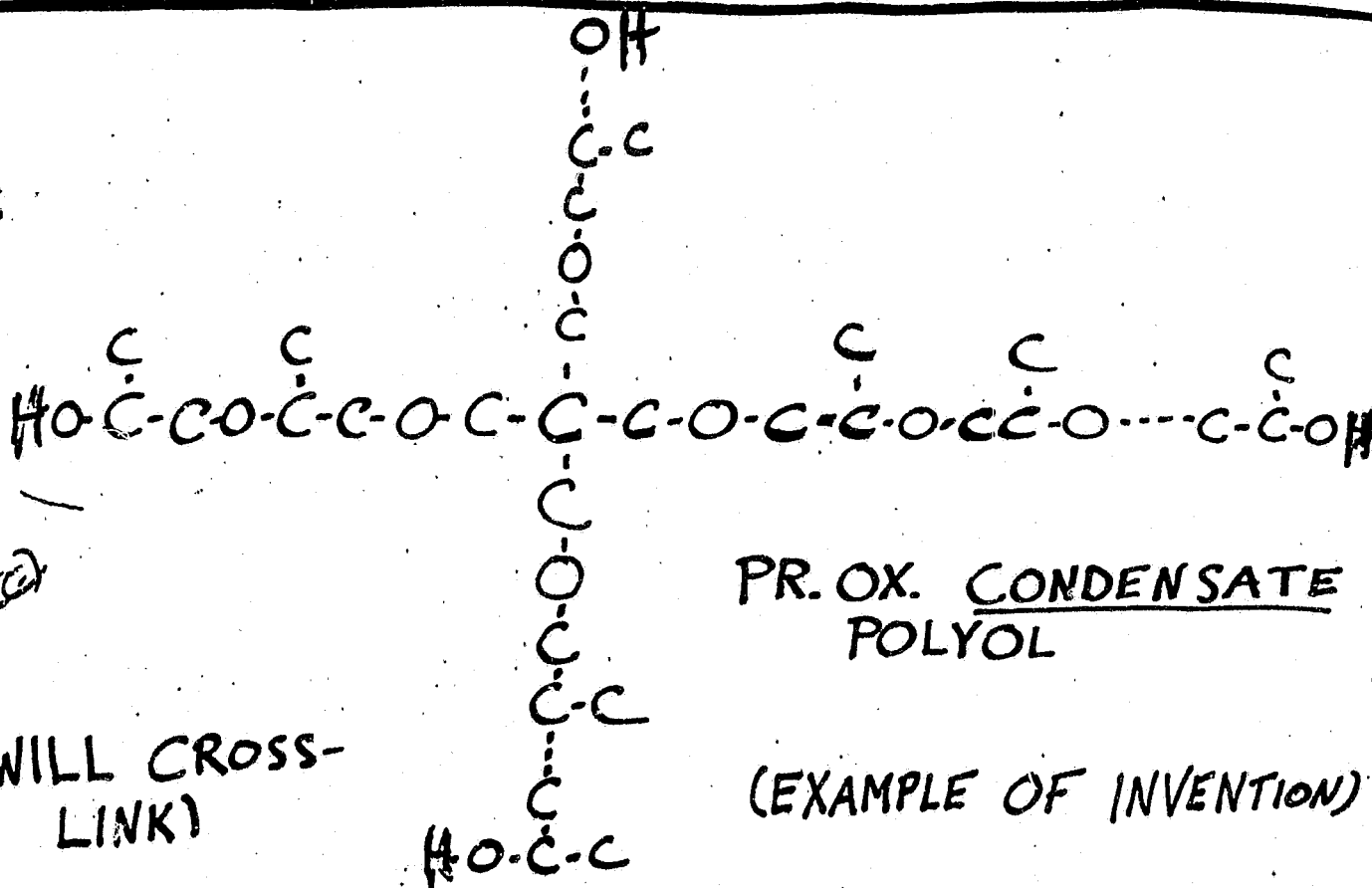


POLYOL - NOT  
POLYETHER

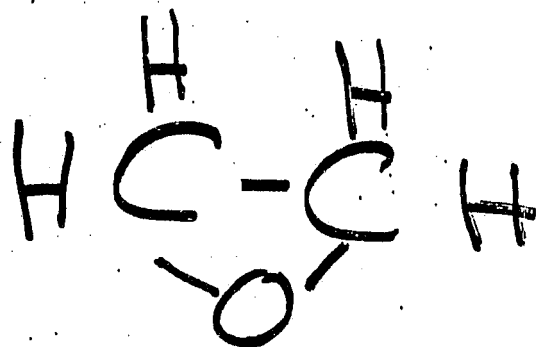
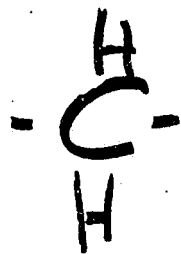
+

POLYETHER  
DIOL

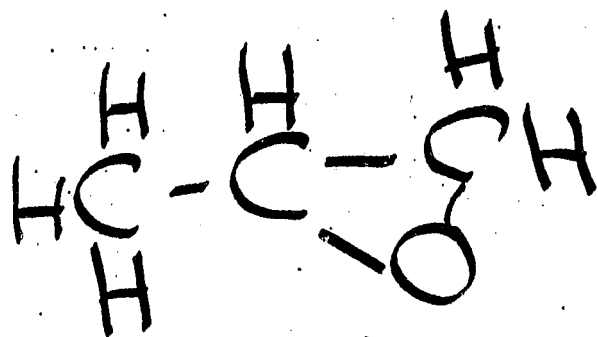
(MIXTURE WILL CROSS LINK)



AJ-3

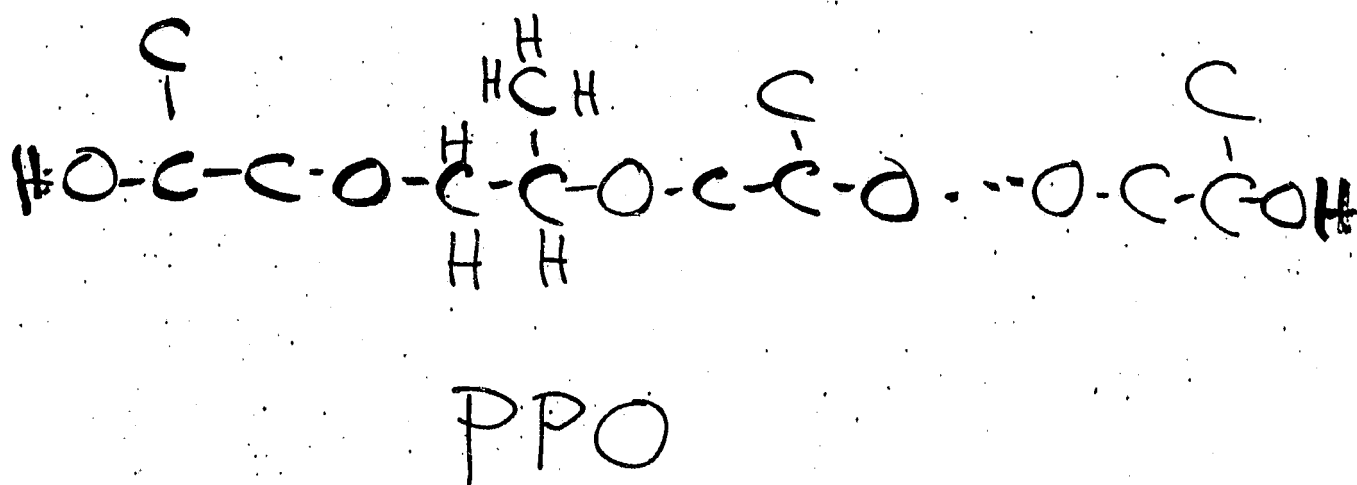
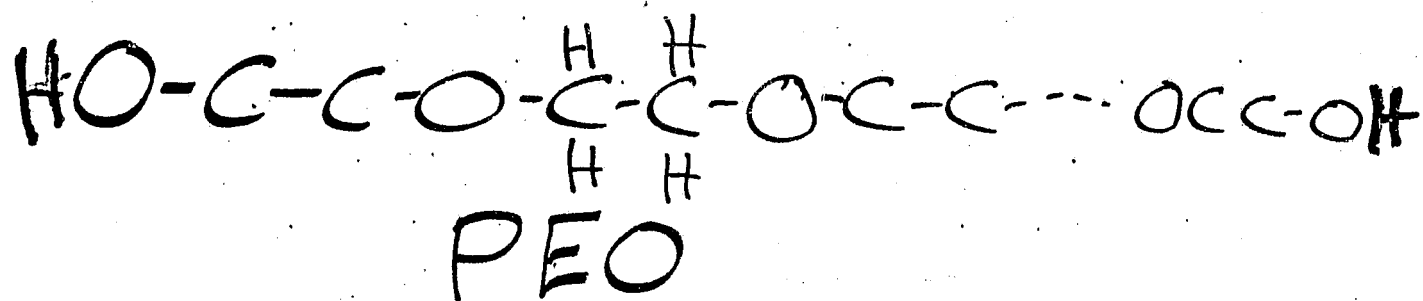


EO

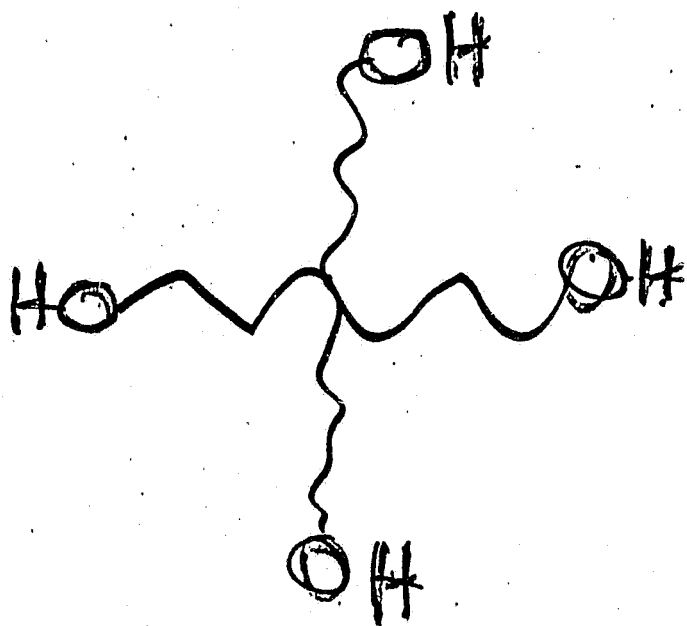


PO

AJ-4



AJ-5



640

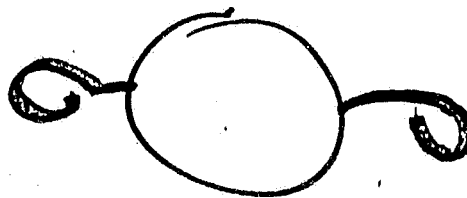
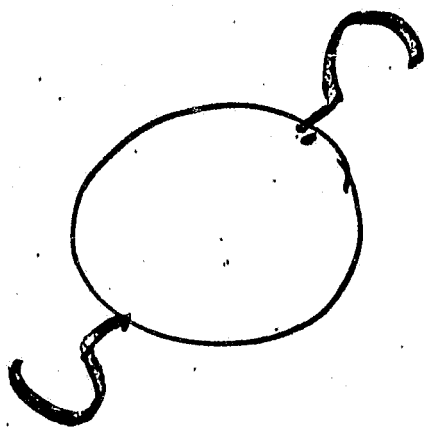
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mod 559

1296

Eq wt = 324

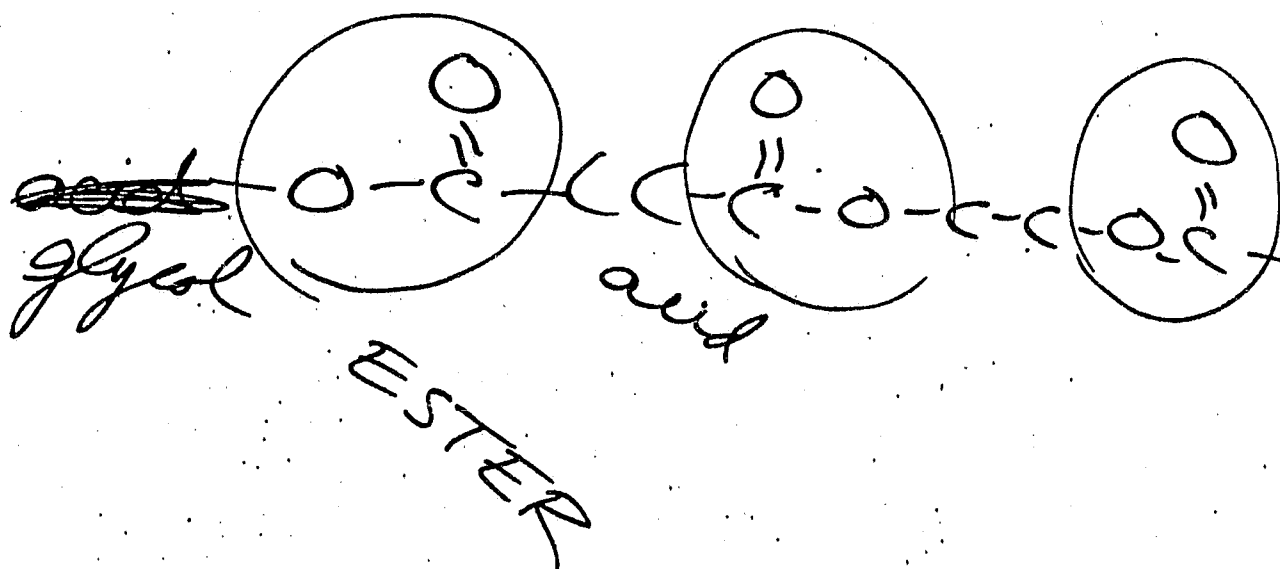
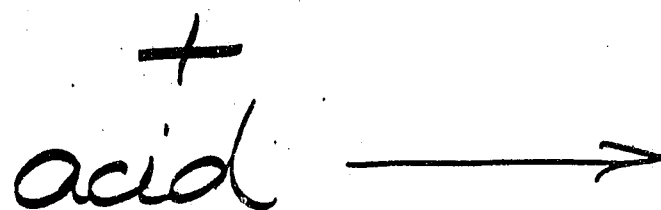
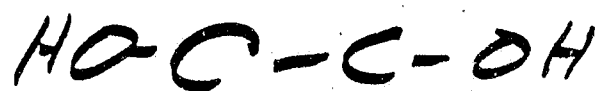
mod 279



174

- Eq. wt. = 87

AJ6



DEFENDANT'S EXHIBIT AK

Defendant's Interrogatories and Plaintiff's  
Answers to Certain of Defendant's Interrogatories

Excerpts - Pages 8

9

11 - 13

30 - 32

42

Pages 1051a to 1059a

Plaintiff's Supplementary Answer:

In addition, Dr. C. M. Greene, 908 Prater Lane, Marion, Virginia.

Defendant's Interrogatory No. 135:

What is the identity sufficient for a motion to produce under Rule 34 F.R.C.P. of all documents relating to knowledge or use of the invention claimed in U.S. Letters Patent No. 3,102,875 in this country by others before the invention thereof by Heiss?

Plaintiff's Answer:

Pursuant to the option offered by Jefferson in its set of interrogatories, and in lieu of identification of documents in response to this interrogatory, General will allow Jefferson, by its attorneys, to inspect and make copies of the documents requested to be identified.

Defendant's Interrogatory No. 136:

Referring to paragraphs 8(a) and 8(b) of the Complaint what is the identity, sufficient for a motion to produce under 34 F.R.C.P., of the patents and printed publications in which the invention was patented or described?

Plaintiff's Answer:

Pursuant to the option offered by Jefferson in its set of interrogatories, and in lieu of identification of documents in response to this interrogatory, General will allow Jefferson, by its attorneys, to inspect and make copies of the documents requested to be identified.

Defendant's Interrogatory No. 137:

Referring to paragraph 8(b) of the Complaint:

(a) when, where, by whom and in what manner was the invention in public use or on sale, specifying the chemical composition of the polyurethane material produced, the method used to produce the polyurethane material, and the chemical name and amount of each ingredient used in making the polyurethane material?

(b) what was the trade name or other designation of each method and/or product in public use and/or on sale?

(c) what is the name and address of each person having knowledge of such public use or sale?



Plaintiff's Answer:

This information has not been ascertained but will be the subject of discovery.

Defendant's Interrogatory No. 138:

What is the identity, sufficient for a motion to produce under Rule 34 F.R.C.P., of any documents relating to the public use and/or sale referred to in the answer to Interrogatory No. 137?

Plaintiff's Answer:

Same as Interrogatory No. 137.

Defendant's Interrogatory No. 139:

Referring to paragraph 8(c) of the Complaint, what is the identity of the patents and applications, sufficient for a motion to produce under Rule 34 F.R.C.P.?

Plaintiff's Answer:

Pursuant to the option offered by Jefferson in its set of interrogatories, and in lieu of identification of documents in response to this interrogatory, General will allow Jefferson, by its attorneys, to inspect and make copies of the documents requested to be identified.

Defendant's Interrogatory No. 140:

Referring to paragraph 8(d) of the Complaint, what is the basis for the statement that Heiss did not himself invent the subject matter?

Plaintiff's Answer:

As presently advised, and subject to further discovery, the prior art patents and publications and prior invention of Dr. Charles C. Price and the documents that will be produced as set forth in answer to Interrogatories Nos. 134, 139 and 147.

Defendant's Interrogatory No. 141:

Referring to paragraph 8(d) of the Complaint, what is the identity, sufficient for a motion to produce under Rule 34 F.R.C.P., of any documents relating to the statement that Heiss did not himself invent the subject matter?

Plaintiff's Answer:

Pursuant to the option offered by Jefferson in its set of interrogatories, and in lieu of identification of documents in response to this interrogatory, General will allow Jefferson, by its attorneys, to inspect and make copies of the documents requested to be identified.

allow Jefferson, by its attorneys, to inspect and make copies of the documents requested to be identified.

Plaintiff's Supplementary Answer:

In addition to the patents previously identified and furnished to defendant, plaintiff relies on the following United States Patents:

<u>Patent No.</u>	<u>Patentee</u>	<u>Date Granted</u>
1,922,459	Schmidt et al.	Aug. 15, 1933
2,527,970	Sokol	Oct. 31, 1950

Plaintiff's Supplementary Answer No. 2:

In addition to art previously identified and furnished to defendant, plaintiff relies on the following:

U. S. Patent No. 2,577,281

Angewante Chemie, 59, ps. 257-272 (1947)

Monsanto Dep. Ex. 6 - translation of above article

Defendant's Interrogatory No. 147:

Identify the part or parts of the invention which do not constitute patentable invention in view of prior art, as alleged in paragraph 8(g) of the Complaint, including identity of the specific prior art relied on and the manner in which each piece of prior art serves to defeat invention in each instance.

Plaintiff's Answer:

The process purported to be defined by claims 3-6, 8, 10 and 11 of Heiss patent No. 3,102,875 and the product purported to be defined by claim 9 do not constitute patentable invention. The prior art includes:

(1) Prior invention by Dr. Charles C. Price of polyurethane products formed by reacting an organic diisocyanate with condensation products having a molecular weight of at least 600 produced by reacting propylene oxide with polyhydric alcohols having 3 or 4 hydroxyl groups in a proportion providing an excess of -NCO groups over the reactive hydrogen groups of the condensation product.

(2) U. S. Patent No. 2,284,896 - Discloses polyurethane resins formed by reacting organic diisocyanates with polyhydric alcohols, including trihydric alcohols, e.g., glycerol and triethanolamine.

(3) U. S. Patent No. 2,511,544 - Discloses high molecular weight polyurethane products formed by reacting polyols containing at least 2 hydroxyl groups, including polypropylene glycols, with an organic diisocyanate in an amount providing an excess of -NCO groups over the reactive hydrogen groups of the polyol.

(4) U. S. Patent No. 2,692,874 - Discloses polyurethane products formed by reacting a polyalkylene ether glycol, including polypropylene ether glycols, with an organic diisocyanate, e.g., toluene diisocyanate and water in proportions providing an excess of -NCO groups over reactive hydrogen groups.

(5) U.S. Patent No. 2,726,219 - Discloses polyurethane foams produced by reacting polypropylene ether polyols, e.g., polypropylene glycol, with organic diisocyanates, e.g., toluene diisocyanate, and water in a molar ratio of diisocyanate to the polypropylene ether polyol providing a ratio of NCO to active hydrogen groups in the ratio of between 1.5:1 and 4.5:1.

(6) U. S. Patent No. 2,787,601 - Discloses polyurethane products formed by reacting castor oil with organic diisocyanates, e.g., toluene diisocyanates, and water. The ratio of reactants provides a ratio of -OH groups to -NCO groups leaving 52.5-77.5% isocyanate groups unreacted.

(7) U. S. Patent No. 2,855,421 - Discloses polyurethanes formed by reacting polyhydric alcohols, including glycerol, trimethylol ethane, trimethylol propane, 1,2,4-trihydroxy butane, pentaerythritol and triethanolamine with diisocyanates, e.g., toluene diisocyanate, to form adducts containing free -NCO groups and which are converted to insoluble high molecular weight polyurethane resin products by reaction of polyhydroxy compounds, water or other active hydrogen containing compounds.

(8) U. S. Patent No. 2,948,691 - Discloses the production of polyether polyurethanes by reacting a polyether polymer produced by condensing alkylene oxides with aliphatic polyhydric alcohols, including alcohols having less than 7 carbon atoms and containing 3 to 4 hydroxyl groups, e.g., trimethylol propane and pentaerythritol, with an organic diisocyanate. An excess of organic diisocyanate is utilized to provide an excess of NCO groups over the reactive hydrogen group contained in the polyalkylene ether polyol. These materials are mixed and reacted to form a polyurethane product having a chain length substantially greater than the chain length of the polyether polymer condensation product.

(9) "Manufacture and Use of Some German Synthetic Adhesives and Raw Materials", B.I.O.S. Final Report No. 456, Item No. 22, January 1946, pages 27032 - Discloses a product (Desmodur TH) produced by reacting toluene diisocyanate with a polyhydric alcohol (trimethylol propane) in proportions providing an excess of -NCO groups over reactive hydrogen groups to form an adduct containing free isocyanate end groups. This adduct is further reacted with active hydrogen materials to form high molecular weight polyurethane reaction products.

(10) "German Plastics Practice", DeBell, 1946, pages 301-302 - Discloses the production of polyurethane products (Desmodur HH and Desmodur TH) formed by reacting organic diisocyanates (1,6-hexamethylene diisocyanate and toluene diisocyanate) with trimethylol propane in amounts providing an excess of -NCO groups over reactive hydrogen groups to form a partially polymerized product. This product is formed into an insoluble polyurethane polymer product by completing the condensation with such polyfunctional alcohols as glycerine and trimethylol propane.

(11) "Chemical Engineering", Vol. 57, No. 4, April 1950, pages 165-166 - Discloses polyurethane products formed by reacting castor oil, -- a trihydroxy alcohol, -- with toluene diisocyanate.

Plaintiff's Supplementary Answer:

Each of the said patents identified in the Supplementary Answer to Interrogatory No. 146 discloses condensation products of alkylene oxides, including ethylene oxide and propylene oxide, and polyhydric alcohols having 3 to 4 hydroxyl groups. These condensation products, including the propylene oxide condensates which are set forth in the claims of Heiss patent No. 3,102,875, are referred to in Windemuth patent No. 2,948,691 and are prior art polyglycol ethers suitable for reaction with diisocyanates to produce polyurethane reaction products.

Plaintiff's Supplementary Answer No. 2:

U. S. Patent No. 2,577,281 discloses polyurethane groups, including three hydroxyl groups, with polyisocyanates.

Angewante Chemie describes the reaction scheme of the Heiss claims. It describes reacting compounds containing three or more hydroxyl groups with polyisocyanates to produce polyurethane products. Compounds containing three or more hydroxyl groups include compounds such as condensate of propylene oxide with polyols containing three or four hydroxyl groups.

Defendant's Interrogatory No. 148:

Referring to paragraph 8(h) of the Complaint:

(a) Identify the part or parts of U.S. Letters Patent No. 3,102,875, by column and line, which are not described in full, clear, concise and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the invention thereof.

(c) The persons named in or connected with the preparation and prosecution of the Heiss patent application; General's attorneys; Mobay personnel and representatives presently unknown to General; and others having knowledge of the existence of the claims set forth in U. S. Patent Nos. 2,948,691 and 3,102,875 presently unknown to plaintiff.

Defendant's Interrogatory No. 231:

What is the name, address, present position and employment of each individual who supplied any information included in the answers to the above interrogatories, and identify each answer and the information therein supplied by such individual.

Plaintiff's Answer:

Frank C. Rote, 1 General Street, Akron, Ohio supplied information for the answers to Nos. 165, 185-187, 190-192 and 213.

Watson Leavenworth Kelton & Taggart, General's attorneys, 100 Park Avenue, New York, New York supplied information for answers to all other interrogatories.

Defendant's Interrogatory No. 232:

From 1954 until about December 1956 did plaintiff make polyesterurethane foam on a commercial basis?

Plaintiff's Answer:

Yes.

Defendant's Interrogatory No. 233:

From 1954 until about November 1956 did plaintiff make polyetherurethane foam on a commercial basis?

Plaintiff's Answer:

No.

Defendant's Interrogatory No. 234:

When did the plaintiff begin preliminary production, including trial runs and commercial runs, of diol polyether prepolymer flexible urethane foam and until when did the commercial production continue?

Plaintiff's Answer:

Began about November 1956 and continued to the end of 1958. Commercial production of this type of foam continues to this day on an intermittent basis.

Defendant's Interrogatory No. 235:

If plaintiff is no longer producing the urethane foam referred to in Interrogatory No. 234 on a commercial basis, why was the commercial production of such foam discontinued?

Plaintiff's Answer:

See Answer to Interrogatory No. 234. The foam referred to in Interrogatory No. 236 was adopted primarily because of improved economics and the commercial availability of propylene oxide based triols of urethane grade.

Defendant's Interrogatory 236:

When did plaintiff begin producing one-shot flexible polyetherurethane foam using propylene oxide based triols, when was this foam first produced on a commercial basis, and until when did such commercial production continue?

Plaintiff's Answer:

Production trial runs commenced about September 1958 and ended about July 1959. During this period of time some of the foams from the trial runs may have been sold. Commercial production continues to this day.

Defendant's Interrogatory 237:

If plaintiff is no longer producing the urethane foam referred to in Interrogatory No. 236 on a commercial basis, why was the commercial production of such foam discontinued?

Plaintiff's Answer:

Not applicable.

Defendant's Interrogatory No. 238:

Since September 3, 1963, the issue date of the Heiss patent, did the commercial production of flexible polyetherurethane foams by plaintiff constitute infringement of one or more claims of United States Letters Patent No. 3,102,875?

Plaintiff's Answer:

For the purpose of this lawsuit, plaintiff states that, if U. S. Patent No. 3,102,875 is valid, the commercial production of certain of its flexible polyether urethane foam would constitute a literal infringement of claims 3, 4, 5, 6, 8, 9, 10 and 11 of said patent. (See paragraph 7 of Amended Complaint)

Defendant's Interrogatory No. 239:

From 1964 to date has plaintiff manufactured in excess of 100 million pounds of the flexible polyether urethane foam in infringement of United States Letters Patent No. 3,102,875?

Plaintiff's Answer:

From 1964 to date plaintiff has manufactured in excess of 100 million pounds of the flexible polyether urethane foam referred to in Interrogatory No. 238.

\* \* \* \*

Defendant's Interrogatory No. 247:

On what date does Plaintiff contend that Defendant's misuse of Heiss U. S. Patent No. 3,102,875 (hereinafter referred to as the "Heiss patent") commenced?

Plaintiff's Answer:

January 26, 1966.

Defendant's Interrogatory No. 248:

Does Plaintiff contend that Defendant is presently misusing the Heiss Patent?

Plaintiff's Answer:

Yes.

Defendant's Interrogatory No. 249:

What acts of Defendant constituted or are constituting the alleged misuse of the Heiss patent, identifying the nature, date and place of each act and all persons involved with respect to each act?

Plaintiff's Answer:

Plaintiff is still investigating this defense and expects to examine defendant thereon. In addition, the infringement action asserted by defendant against plaintiff.

Defendant's Interrogatory No. 307:

If the Answer to Interrogatory No. 306 is in the affirmative, what is the date, place and manner of each such discussion, including an identification of the discussion, including an identification of the discussion as written, oral, by phone or in person?

Defendant's Interrogatory No. 308:

If the Answer to Interrogatory No. 306 is in the affirmative, what is the identity of each person present or participating in the discussion?

Defendant's Interrogatory No. 309:

If the Answer to Interrogatory No. 306 is in the affirmative, what is the identity, sufficient for a request for production under Rule 34 F.R.C.P. of all documents relating or referring in any manner to such discussions and/or the matters discussed?

Plaintiff's Answers:

Several oral discussions were had between Frank Rote and Clellie Upchurch during which the Jefferson-Mobay Agreement may have been mentioned. There are no documents relating to such discussions except outside counsel's memoranda for which privilege is claimed.

312. Referring to Plaintiff's Answer to Interrogatory No. 147, of the eleven instances of prior art listed, which one does General Tire contend to be the best prior art against the Heiss patent and what is the basis for such contention?

ANSWER

Plaintiff's counsel has not yet determined which is the "best" prior art.

Plaintiff's Supplementary Answer:

Plaintiff's counsel believes that the "best" prior art is the Price work and the Windemuth '691 patent.



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